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ON THE FORMATION, DECOMPOSITION AND GERMICIDAL ACTION OF BENZOYL ACETYL AND DIACETYL PEROXIDES.

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Hoitsema[1] has shown that the amount of hydrogen dissolved in palladium is, within certain limits, directly proportional to the pressures exerted, but if these are very small, then the quantity is proportional to the square root. The conclusion to be reached is, therefore, that, under these conditions, the hydrogen is present in the form of individual atoms. The formation of water from hydrogen and oxygen, under ordinary conditions, takes place with unmeasurable slowness, but is increased to measurable rapidity by the presence of certain substances, so that with finely divided metals, such as platinum or palladium sponge, the rate of change is often so rapid that explosion may occur. Unquestionably, in these cases, the metal has a specific action, but the intensity of this is increased by increasing the surface. The gases in these cases are, perhaps, best considered as being in solution in the solids, and the dissociating action of solvents would produce

[1] Ztschr. physik. Chem., 17, 1.

the monatomic condition made apparent by Hoitsema. Mond, Ramsay, and Shields[1] have shown that palladium foil, sponge, or black take up equal quantities of hydrogen, so that the solubility of the gas is independent of the surface. The hydrogen in these solutions has the characteristics of a metal, and observing the analogy between this and fluid solutions of one metal in another, it also seems probable that the hydrogen is in the form of individual atoms. The increased activity can be explained not only by the greater concentration of hydrogen in unit space, but also by the dissociation which has taken place. The resistance to the oxidation of gaseous hydrogen may rest upon the slow rate at which the molecules are split into atoms, and this dissociation takes place more rapidly in metallic solution, thus accounting for the increased rate of oxidation. The same must be true, to a greater or less extent, of all surfaces, although not all have the same solvent or dissociating power for hydrogen.

In the case of oxygen there is no such marked absorption by metals, so that instances in which oxygen is undoubtedly rendered active by the presence of catalyzers are not frequent. The change from sulphur dioxide to sulphur trioxide by the action of platinized asbestos or platinum is unquestionably an example.[2] The oxidation of mixtures of benzaldehyde and acetic anhydride, when spread on sand and exposed to the air, produces, according to the conditions, either benzoyl peroxide[3] or benzoyl acetyl peroxide.[4] These reactions were, in our opinion, also cases in which the catalytic action of the solid surface brought about the oxidation, so that, while undertaking some bacteriological studies on the action of organic peroxides, we also studied the influence of catalytic agents on the formation of this class of bodies.

Nef has shown that the formation of benzoyl acetyl peroxide (accompanied by that of benzoyl acetyl oxide and benzoic acid), is much more rapid when the mixture of benzaldehyde and acetic anhydride is spread upon sand than when it is exposed to the air in glass vessels; this acceleration, in his

[1] Proc. Roy. Soc., **62**, 290.

[2] For an extended review of this subject see Bodländer's Ahrens Vorträge, **3**, 385.

[3] H. Erlenmeyer, Jr.: Ber. d. chem. Ges., **27**, 1959.

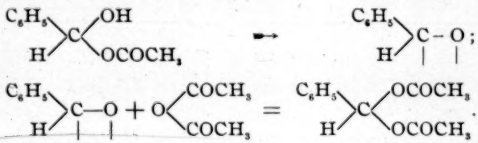
[4] Nef: Ann. Chem. (Liebig), **298**, 280.

paper, is tacitly ascribed simply to mechanical causes, owing to the greater ease of contact between the air and the mixture. In order to determine whether the contact of a sufficient volume of air is alone necessary for rapid peroxide formation, or whether the surface action of a solid is necessary, we performed the following experiments:

Fifty grams of benzaldehyde and 50 grams of refractioned acetic anhydride were placed in an ordinary gas washing-bottle, the entrance tube of which was drawn out to a number of capillaries, so as to insure a very fine division of the air bubbles. This wash-bottle was placed in a freezing-mixture and air, previously cooled by passing th rough a worm and drying bottle with concentrated sulphuric acid, both packed in a freezing mixture, was passed through in a rapid stream for seven hours, at the end of which time the contents of the bottle suddenly solidified. The crystals were separated and recrystallized from petroleum ether, when they proved themselves to be pure benzylidene diacetate. The yield was only a little less than quantitative, and only minimal quantities of either benzoyl acetyl peroxide or benzoic acid were formed. Repetition of the experiment, at the same temperature, produced the same result. At higher temperatures (13° to 14°), even after a current of air had freely passed for twenty-four hours, only a trace of peroxide was produced, but at the same time no benzylidene diacetate, or at least no quantities sufficient for isolation from the mixture in the flask, could be observed. The benzaldehyde and acetic anhydride were almost completely unchanged. The rapid formation of benzylidene diacetate, therefore, seemed to be dependent upon the condition of low temperature. The result shows that, when the mixture of benzaldehyde and acetic anhydride is kept agitated by a rapid current of nearly dry air, the formation of benzylidene diacetate is much more rapid than when the mixture is left standing alone, for Nef[1] found only 2 grams of benzylidene diacetate formed from 48 grams of benzaldehyde, even after five days' standing. In Nef's experiments a large quantity of acetic acid (24 grams) was added, whereas in the above, the acetic anhydride was twice refractioned, and so could contain

[1] Ann. Chem. (Liebig), **298**, 278.

only a trace of acetic acid. A large quantity of acetic acid, therefore, has no influence in increasing the rate of action, but on the contrary it seems to diminish it. If Nef's assumption that the formation of benzylidene diacetate is due to a previous addition of acetic acid, separation of the latter to form nascent benzaldehyde, and subsequent addition of acetic anhydride, is correct :



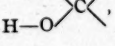
Then the increase in the concentration of the acetic acid should accelerate rather than retard the rate of reaction.

In order to test whether substances other than acetic acid would also affect the rate of formation of benzylidene diacetate, 10 grams of aldehyde and 10 grams of refractioned acetic anhydride were placed in a tube with a strip of platinum foil, 1 cm. wide and 5 cm. long, and dry air was run through for twenty hours. The current was very slow, so as to secure merely an agitation of the liquid. At the end of this time 16.5 grams of benzylidene diacetate had been formed ; calculated 19.5 grams. By far the greater portion of this diacetate was produced in the first hour, and the tube at the beginning became quite warm, showing that under these conditions the addition of acetic anhydride to benzaldehyde is much accelerated, although only a trace of acetic acid could be present. On repeating the above experiment, all conditions being the same except that the tube was cooled to 10°, the formation of the diacetate was retarded so that the change was not complete for three days. The same mixture, sealed in a tube and placed in the shaking machine, solidified completely, forming benzylidene diacetate after seven hours, so that agitation by means of a current of air did not accelerate the reaction. Other metals have even a more marked effect. Zinc and tin, when placed in tubes containing the mixture of aldehyde and anhydride, effect the change in about half an hour, with a

slow current of air passing through, and with iron the reaction-products become heated at once, and the addition is complete after a few minutes.

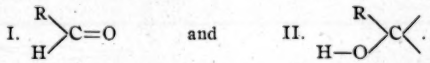
Various metals, therefore, exert a marked catalytic action on the formation of benzylidene diacetate, independently of the amount of acetic acid which may be present. Acetic acid, however, may act as a catalytic agent, increasing the velocity of the reaction, but not altering the final equilibrium. Indeed, in accordance with Nef's results, we have found that acetic anhydride which had been freed from acetic acid by standing over sodium and then distilling, did not form benzylidene diacetate in appreciable quantities, with iron and a slow current of air, until thirty-six hours had elapsed. And probably, as in Nef's case, mixtures of benzaldehyde and acetic anhydride, purified in this manner, if simply standing in a closed flask, would react with such extreme slowness that amounts of benzylidene diacetate sufficient for isolation would not be produced for months. We have not completed our work on the action of catalysis in the formation of benzylidene diacetate, as very slight variations in the purity of the materials or of the catalyzers produce such marked variations in the rate of formation that concordant results are difficult to obtain. Neither have we determined whether a mixture of benzaldehyde and acetic anhydride, purified by standing over sodium, will eventually produce benzylidene diacetate, but the work has gone far enough to demonstrate that various substances have different effects on the rate of addition, and that even traces of acetic acid are just as effective as the large amounts used by Nef.

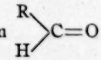
The conclusion, therefore, is that the action of acetic anhydride on benzaldehyde is purely one of addition, and that the course of the reaction is simpler than the one proposed by Nef. It is nevertheless probable, in view of the work of Baeyer and Villiger[1] on benzoperacid and on the oxidation of benzaldehyde, as well as the other additive reactions in which benzaldehyde takes part, that a methylene derivative,

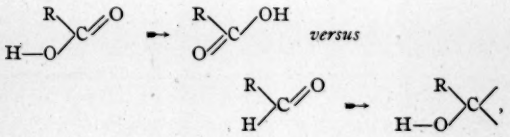


[1] Ber. d. chem. Ges., 33, 1582.

takes part in the reaction. Many changes which aldehydes undergo can best be explained by the existence of an equilibrium between the two isomers



Only a trace of the enol form (II.) need be present to start reactions. As soon as form II. is removed, the equilibrium is restored by a renewed change from I. (keto form) to II. (enol form), and so on until reaction is complete. The ease with which the change can be brought about would determine the rate at which a given aldehyde would react. The existence of an equilibrium between keto and enol form in acetoacetic ether is now extremely probable, in view of the work of Schiff,[1] as well as the large mass of modern literature on desmotropic forms of substances, which seems to show that an equilibrium between the two forms exists in many liquid aldehydes and ketones. This view need only be extended to ordinary aldehydes of the form  to have a rational explanation of the various reactions of this class of bodies. Catalyzers, as in the above case of the formation of benzylidene diacetate, would then simply affect the rate of change of keto to enol form, on exactly the same principle as we suppose that catalyzers can increase the rate of dissociation of the hydrogen molecules into atoms in the formation of water.[2] The relative inactivity of the carbonyl oxygen atom in the carboxyl group



would thus be explained by the mere fact that two distinct forms, one of which is the intensely reactive unsaturated form, and the consequent equilibrium are not possible, and

[1] Ber. d. chem. Ges., 31, 205, and following.

[2] Bodländer: Ueber langsame Verbrennung, Ahrens Vorträge, 3, 439.

hence carbonyl in the carboxyl group cannot behave like carbonyl in aldehydes and ketones.

As the rapid formation of benzylidene diacetate, provided acetic anhydride, which has merely been refractioned, is used, causes the contents of the tubes through which air is passed to solidify before appreciable quantities of peroxide are formed, we were compelled, in all experiments relating to the influence of surface on the rate of oxidation, to use acetic anhydride which had stood over sodium for some time, and which was then poured off and refractioned. By this means the formation of benzylidene diacetate is so greatly retarded that, in most cases, we were able to run air through the mixture of benzaldehyde and acetic anhydride long enough to obtain quantities of benzoyl acetyl peroxide which could be quantitatively determined.

The problem of ascertaining the amount of peroxide which is present in a mixture of benzaldehyde, acetic anhydride, acetic acid, benzylidene diacetate, and benzoyl acetyl oxide, all of which bodies must be present in the reacting liquid after air has been run in for a sufficient length of time, is not an easy one, and we soon discovered that such means as decolorizing indigo or titration with potassium iodide could not give accurate results. We finally adopted the method of heating a measured quantity of the mixture resulting from oxidizing benzaldehyde and acetic anhydride by means of a current of air and measuring the evolved gas. That this gives a reasonably accurate means of quantitatively determining benzoyl acetyl peroxide in the presence of all of the other substances occurring during the reaction is shown by the following experiments:

A weighed quantity of benzoyl acetyl peroxide was dissolved in about 5 cc. of benzaldehyde and the solution placed in a small, round-bottomed flask, which was connected with a carbon dioxide apparatus on the one side and a Schiff's azotometer on the other. After all air had been expelled the flask was heated with a free flame until evolution of gas began, then the flame was removed, and only brought under the flask from time to time, as the reaction required. The decomposition must take place as rapidly as possible, without causing explosion.

Gram peroxide used.	Calculated gas volume for 1 molecule gas per 2 molecules peroxide.	Found.
0.2445	15.1	14.3
0.1199	7.4	7.3
0.2084	12.9	12.7
0.2018	12.5	12.3
0.0941	5.8	6.0
0.3306	20.5	21.2

As will be seen from the above, 1 molecule of gas is developed for every 2 molecules of peroxide, and the method is sufficiently accurate for all purposes of measurement. No gas whatever is obtained on heating pure benzaldehyde or a mixture of benzaldehyde and acetic anhydride, or any other mixture not containing peroxide under the above conditions, as we have proved to our satisfaction. The gas collected over potash, much to our surprise, proved to be methane.

The gas collected from 5 grams of benzoyl acetyl peroxide was allowed to stand over strong potash solution for twenty-four hours and was then analyzed by combustion.

	Calculated for CH_4.	Found.
C	75.0	75.4
H	25.0	24.6

A gas analysis, kindly carried out by Mr. White, of this laboratory, by the usual methods, confirmed the combustion and proved the gas to be methane. The gas does not reduce a solution of palladium chloride, hence no hydrogen is present.

If the gas given off by heating benzoyl acetyl peroxide is collected over mercury, then the volume is equal to that calculated for 4 molecules of gas for every 2 molecules of peroxide decomposed, and of these four molecules three are carbon dioxide.

I. 1.111 grams substance in 40 cc. of xylene were decomposed by heating to 105° in an oil-bath, the temperature being gradually increased to 155°, and the total gas collected over mercury. The gas was then passed through a potash bulb by means of a current of air, free from carbon dioxide, and the carbon dioxide weighed. Found 0.379 gram CO_2.

II. 1.238 grams substance in 20 cc. of xylene were decom-

posed as above, care being taken not to heat above 110°. Found 0.431 gram CO_2.

	Calculated for 3 molecules CO_2 to 2 molecules peroxide.	Found. I.	Found. II.
CO_2	36.8	34.1	34.8

The percentage of gas obtained is slightly low, but the decomposition is almost quantitative. A very minute quantity of benzoyl acetyl peroxide, therefore, decomposes differently. The volume of methane obtained also varies slightly from the calculated. The volume of gas not absorbable by potash varies somewhat if the peroxide is very slowly decomposed in xylene, but is fairly constant, as shown above, if the substance is heated over a free flame.

Two molecules of benzoyl acetyl peroxide, therefore, decompose into 3 molecules of carbon dioxide, 1 of methane, and a liquid residue. The empirical equation would be:

$$2C_9H_8O_4 = 3CO_2 + CH_4 + C_{14}H_{12}O_2.$$

The high-boiling residue was examined as follows: The xylene was distilled under diminished pressure from the residue obtained by heating 5 grams. The remainder was then taken up in ether and extracted with sodium carbonate. On acidifying the carbonate, 0.11 gram of an acid was isolated. This acid has not been identified. The ether was then distilled off and the non-acid remainder boiled for six hours on a water-bath with 2 grams of alcoholic potash. The alcohol was then distilled off and the whole taken up in water. The non-saponifiable portion was carefully extracted with ether. The alkaline solution, when acidified, gave 0.7 gram of benzoic acid. The non-saponifiable portion was fractioned at 18 mm. pressure. Two grams went over between 160° and 185°, and about an equal weight of high-boiling residue, which would not distil up to 265°, remained. The distillate is colorless and boils between 260° and 285° at ordinary pressure. It cannot be crystallized. No constant-boiling product could be obtained from it. An analysis showed this remainder to be a mixture of high-boiling hydrocarbons.

Weight of substance 0.1332.

	Found. Gram.	Per cent.
H	0.0114	8.5
C	0.1193	89.6
Total,	0.1307	98.1

The hydrocarbons have not, as yet, been identified. The 2 grams of high-boiling residue finally passed over when heated with a free flame, leaving practically no residue, when the thermometer finally rose to 335°. This high-boiling portion is not a hydrocarbon.

The result shows that, while the gaseous products are related to the original body in a very simple manner, the liquid remainder is by no means as simple. A large portion consists of hydrocarbons of high boiling-point, so that the result of the decomposition has been the coupling of the residues. The saponifiable portion, which yields the benzoic acid, is probably phenyl benzoate. Hitherto the amount of substance at our disposal has been too small to follow out this interesting decomposition in such a way as to identify the liquid portion, but we intend to return to this question in the near future, and clear up the mechanism of this change as well as the decomposition of other peroxides by heat, for the reaction may be made one of great synthetic importance. The simplest change,

$$\begin{matrix} C_6H_5CO.OO.COCH_3 \\ C_6H_5CO.OO.COCH_3 \end{matrix} \longrightarrow \begin{matrix} C_6H_5CO.O \\ C_6H_5CO.O \end{matrix} \begin{matrix} O.COCH_3 \\ O.COCH_3 \end{matrix} \longrightarrow$$

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix} \begin{matrix} CO\ O \\ CO\ O \end{matrix} \begin{matrix} O\ CO \\ O\ CO \end{matrix} \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

by which diphenyl and ethane would be produced, does not take place, and it is a remarkable fact that the methane, which must unquestionably be produced from one of the methyl groups by reduction of a second methyl group, should result at all, in preference to ethane. The further study of the decomposition-products will probably do much to clear up the constitution of organic acid peroxides.

The above results having fully established the feasibility of determining the quantity of benzoyl acetyl peroxide which can be produced by passing air through a mixture of benzal-

dehyde and acetic anhydride, we first made the following blank test:

Twelve test-tubes were each filled with a mixture of 5 grams of benzaldehyde and 5 grams of acetic anhydride, both dry, and a current of thoroughly dried air was slowly passed through all the tubes at once, placed in series. The first six tubes were opened at intervals of one-half hour, and the contents tested for peroxide. The amount scarcely increased after the first half hour, when 1 cc. of gas only could be collected. One of the tubes was then opened and a small piece of filter-paper, from which the fat had been extracted, placed in it, with the result that the peroxide production increased by 200 per cent in two hours. The tubes which had run for about eighteen hours finally solidified to benzylidene diacetate. This test shows that, unless surfaces other than those of the test-tube and delivery-tube are present, the production of peroxide is very slow, despite the large quantity of air which is run through in six hours. An equilibrium is finally reached in which peroxide is destroyed as fast as it is formed. The paper surface instantly produces a marked increase.

The same series of tubes were now cleaned thoroughly, dried, and each filled again with the same mixture. Pieces of pure metal, in strips, were now dropped in, care being taken to have the surface approximately the same in all, and the strips so placed that the entering air would come in contact with them. The current was admitted during fifteen hours, temperature 12°, when the tubes were taken out, the air stopped, and the peroxide present in each estimated in turn. By this method the tube opened last stood twelve hours, without air being admitted.

Tube.	Contents.	Gas delivered. cc.	Absolute quantity of peroxide. Gram.
1	Aluminum	12.79	0.2055
2	Extracted filter-paper	10.43	0.1691
3	Blank	4.14	0.0670
4	Magnesium	9.76	0.1580
5	Iron	7.83	0.1267
6	Copper	5.76	0.0732
7	Tin	1.56	0.0256
8	Platinum	0.31	0.0050

The accelerating effect of the surfaces is very apparent in

the first portion of the series, but the gradual decrease of peroxide present the longer the tubes were allowed to stand before determining the gas given off, makes it evident that decomposition of the peroxide takes place, and becomes evident as soon as the current of air ceases. As a consequence we repeated the above series, placing the tubes in the current of air successively after a given interval of time, then allowing each tube to be subjected to the action of air for the same length of time, twenty-two hours and forty minutes, removing each in the order in which it was placed in series, and determining the gas at once. Each tube, therefore, stood the same length of time as all of the others.

Tube.	Contents.	Gas delivered. cc.	Absolute quantity of peroxide. Gram.
1	Aluminum	7.2	0.11656
2	Extracted filter-paper	13.6	0.2201
3	Blank	6.4	0.1036
4	Magnesium	63.2	1.0232
5	Iron	40.5	0.6556
6	Copper	1.7	0.0275
7	Tin	13.4	0.2169
8	Platinum	15.2	0.2460

During this reaction the iron (2.728 grams) lost 0.0064 gram, the aluminum 0.0006 gram from 1.485 grams, and the copper 0.064 gram from 2.366 grams. The copper was decidedly attacked, therefore, whereas all other metals were only altered, if at all, to a slight extent. In order to test whether the fact that the metal was attacked would, in the case of copper, reduce the yield, we carried out a series of experiments with copper alone.

Pieces of copper of equal size, previously completely reduced in a current of hydrogen, were placed in the tubes and the following results obtained :

Time of determination after first admitting air. Hours.	Cc. of gas obtained.
2	2.7
4	6.7
6	4.1
8	3.7
10	3.0
12	2.8
14	2.8
24	2.5

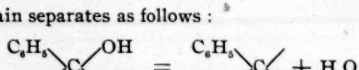
It is evident from this that in the case of copper the formation of peroxide rapidly increases to a maximum, the rate of decomposition then exceeds that of formation until a practical equilibrium is reached after twenty-four hours. The metal is attacked in all cases, but the cause of the decomposition is not to be found in the copper acetate produced, because a tube containing copper acetate only gave 11.9 cc. gas after fifteen hours. This peculiar decomposition of copper will be the subject of future investigations.

The above results show, beyond a doubt, that the rate of formation of peroxide is dependent upon the surface action of substances coming in contact with air and the mixture of benzaldehyde and acetic anhydride at the same time, for the blank tubes, in each case, produce no greater quantity of peroxide than would naturally be expected from the surface of glass exposed. Of all substances used, magnesium seemed to have the greatest effect, so that this metal was used in an experiment carried out with the purpose of determining whether absolutely dry air can form benzoyl acetyl peroxide with a mixture of absolutely dry benzaldehyde and acetic anhydride.

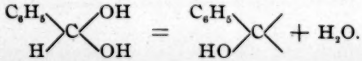
The apparatus consisted of a drying train consisting of a worm tube with sulphuric acid, a tube 3 feet long filled with glass wool dusted over with phosphorus pentoxide, and a tube 4 feet long filled with freshly glowed soda-lime, a reaction tube with the entrance tube for air sealed in and surrounded by a spiral of pure magnesium ribbon, and the exit tube sealed to the side and connected to the aspirator by means of a tube 3 feet long, filled with glass wool and phosphorus pentoxide. The exit tube of the reaction flask was connected by means of a T, with two distilling flasks which were so adjusted that the first and last portions of the distillate could be run off through side stop-cocks, while any quantity of liquid necessary could be introduced into the reaction flask. All parts of the apparatus were sealed together so as to form a continuous piece of glass. The acetic anhydride used was allowed to stand over sodium for several weeks; the benzaldehyde was distilled several times. The apparatus was heated for several hours at 150°, with a current of air passing through, the acetic anhydride and benzaldehyde were then placed in the distilling flasks and

distilled over into the reaction tube, the first portion of the distillate being rejected in each case, and the tube connecting with the apparatus was then fused off. A slow current of air was then passed through for twelve hours.

Ten cc. of mixture gave 12 cc. of gas, corresponding to 0.1952 gram of peroxide. The presence of moisture is, therefore, not necessary in the formation of benzoyl acetyl peroxide. In this experiment 1.234 grams of magnesium were used, which lost only 0.0041 gram during the time of the reaction, and this loss is probably entirely due to the formation of oxide, during the heating and drying, which was removed during the process of cleaning. The magnesium is, therefore, not acted on during the twelve hours of the experiment, although acetic acid must be produced according to any view which we can take of the formation of benzoyl acetyl peroxide from mixtures of acetic anhydride and benzaldehyde. The same result was obtained in other cases when air was run through the mixture for a sufficient length of time to produce acetic acid enough to more than dissolve all the magnesium present. Nef's view[1] of the formation of benzoyl acetyl peroxide supposes that, in the presence of water, benzaldehyde adds the latter to form dioxytoluene:



which again separates as follows:



The latter substance then again acts on water to form orthobenzoic acid and hydrogen:

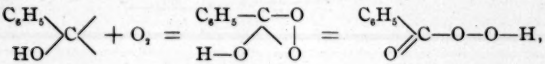
The hydrogen then forms hydrogen peroxide with molecular oxygen, while the benzoic acid forms benzoyl acetyl oxide with acetic anhydride. Finally, hydrogen peroxide is sup-

[1] Ann. Chem. (Liebig), **298**, 280.

posed to oxidize benzoyl acetyl oxide to benzoyl acetyl peroxide.

In view of what has been shown above as regards the ease with which benzaldehyde adds acetic anhydride to form benzylidene diacetate, it seems scarcely credible that, even in the presence of a trace of water, the benzaldehyde should add the latter substance in preference to the former. Nef's view of the mechanism of the reaction must, however, be definitely abandoned after the above demonstration that water is not a necessary factor in the formation of benzoyl acetyl peroxide. The intermediate formation of benzoyl acetyl oxide also does not necessarily accompany the action of air on the mixture of aldehyde and anhydride because, as will be shown below, we have succeeded in so conducting the oxidation as to obtain a crude peroxide which crystallizes completely with only a minimal formation of benzoic acid. Were benzoyl acetyl oxide present in any quantity, it would either manifest itself by being present as an oil mixed with the neutral crystals of peroxide, or, if it were hydrolyzed, its decomposition would show itself by the presence of benzoic acid.

The most reasonable and simple way in which to look upon this oxidation is to assume the existence of an equilibrium between the keto and enol forms of benzaldehyde. The latter would then manifestly add oxygen to form benzoperacid,



which, in turn, would react with acetic anhydride to form benzoyl acetyl peroxide.[1] This view of the reaction would not affect the question as to the structure of benzoperacid, because formula II., which is the more probable one, can easily result from I. by a rearrangement similar to those so frequently observed in organic chemistry. In any event, the structural formulas of hydroperoxide and the organic peroxides are as yet undetermined, although the weight of evidence

[1] Clover, working in one of the laboratories (Freer's), has shown that benzoperacid may be tested for quantitatively by yielding benzoyl acetyl peroxide upon the addition of acetic anhydride. With solutions of the latter peroxide it yields benzoperoxide.

points toward a symmetrical structure, so that this question must be a subject for future investigation. The above results are in accord with those obtained by Baeyer and Villiger[1] on the oxidation of benzaldehyde. The views of Erlenmeyer, Jr.,[2] Jorissen,[3] and Engler and Wild[4] are all based on the supposition that benzoyl peroxide is the result of the oxidation of a mixture of benzaldehyde and acetic anhydride, and are consequently to be rejected because benzoyl peroxide is only a secondary product of the reaction, for we have convinced ourselves that acetic anhydride cannot convert benzoyl peroxide into benzoyl acetyl peroxide. The supposition of Erlenmeyer, Jr.,[5] that possibly an addition-product of benzaldehyde (benzylidene diacetate) is first formed, which latter substance is then oxidized to a substance which is converted by the mixture into benzoyl peroxide and acetic acid is also not correct, for benzylidene diacetate cannot be oxidized to a peroxide either by air or by hydrogen peroxide. The same view in regard to the mechanism of the reaction was advanced by Bodländer[6] and by Michael,[7] both of whom assumed the existence of benzoperacid,

$$C_6H_5CO.O.O.H,$$

before its discovery by Baeyer.

The above experiments also prove conclusively that the formation of peroxides is remarkably accelerated when certain surfaces are present as catalyzers, and that this influence varies with the nature of the surface. In order to prove that the extent of liquid surface exposed is not of influence, a mixture of equal quantities of benzaldehyde and acetic anhydride was placed in a Fernbach flask so that the bottom was covered to a depth of about 3 mm. The flask was allowed to stand for twenty-four hours, at the end of which time only a very small quantity of peroxide had been formed. The same mixture formed in a large, flat watch-glass, and then drained off,

[1] Ber. d. chem. Ges., **33**, 1582.
[2] *Ibid.*, **27**, 1961.
[3] Ztschr. physik. Chem., **22**, 58.
[4] Ber. d. chem. Ges., **30**, 1677.
[5] *Ibid.*, 1961.
[6] Ahrens Vorträge, **3**, 471.
[7] J. prakt. Chem., **60**, 75.

so that a very thin layer was left, so thin that direct contact of the air with the glass surface was possible, was completely oxidized to a mixture of benzoic acid and benzoyl acetyl peroxide within five minutes.

These results prove conclusively that the oxidation of mixtures of benzaldehyde and acetic anhydride cannot be referred in any great measure to a partial dissociation of the ordinary oxygen of the air, as is supposed by van 't Hoff.[1] As this acceleration of the rate of oxidation is brought about by a variety of surfaces, such as sand, paper, cloth, cotton, and various metals, it seems probable that the oxygen of the air, when occluded by any surface, is rendered chemically more active, and this increased activity is due to a partial dissociation of the occluded oxygen molecules

$$O{=}O = \begin{matrix} O{-}O. \\ | \quad | \end{matrix}$$

This view is of great importance from a biological standpoint, as, for example, the ease with which hemoglobin is changed to oxyhemoglobin in the lungs can be referred to the large surface of tissue exposed. If the assumption of an equilibrium between the keto and enol forms is correct, then the difference between the activity of various surfaces can be explained by the assumption that the substances introduced into the mixtures of aldehyde and anhydride have different effects on the rate of change from the keto to the enol form, whereas the surface action on the oxygen remains alike in all.

The above experiments clearly indicated to us the best means of procuring any desired quantity of benzoyl acetyl peroxide.

A mixture of equal weights of benzaldehyde and acetic anhydride is prepared, the mixture placed upon strips of filter-paper or muslin, hung in a large glass jar with a cover, and dry air gradually run through. Care must be taken not to place too many strips in the jar at one time, as contact combined with the rapid formation of peroxide will in a very few minutes bring about local heating to such an extent that the paper chars, and may even take fire. After the odor of benzaldehyde has disappeared, the paper or cloth is extracted with

[1] Ztschr. physik. Chem., 16, 411.

low-boiling petroleum ether, the solution washed with a little soda solution until the washings just become alkaline,[1] then the petroleum ether is partly distilled off from a bath of lukewarm water (the bath must not exceed 80° in temperature, otherwise explosion may result), and the solution is then placed in a freezing-mixture. Crystals of benzoyl acetyl peroxide soon separate, and can be filtered off and recrystallized from the same solvent. On concentrating the petroleum ether further crops of crystals, somewhat less pure, are obtained. The yield often reaches 68 per cent of the theoretical. It varies with the temperature, rate of admission of air, thoroughness of drying, and amount of sunlight. Benzoyl acetyl peroxide thus obtained is identical with that described by Nef. When pure it can be kept apparently indefinitely, provided no moisture comes in contact with it. In the presence of impurities, such as moisture, traces of alcohol, ether, or acids, it gradually decomposes, becoming liquid and then slowly depositing crystals of dibenzoyl peroxide. The liquefaction seems to be due chiefly to a lowering of the melting-point, brought about by the formation of impurities, either diacetyl peroxide or benzoyl hydrogen peroxide, for the melted portion consists for the most part of benzoyl acetyl peroxide. Tubes sealed up, the contents of which had liquefied as above, showed no pressure, so that oxygen is not given off. These changes will be the subject of future investigation. The melting-point of pure benzoyl acetyl peroxide is 40° to 41°.

Pure benzoyl acetyl peroxide is not an oxidizing substance, nor has it any odor, a fact which was also observed by Baeyer.[2] The following experiments will make this clear.

Twenty grams of benzoyl acetyl peroxide were dissolved in 200 cc. of absolute ether, and then 10 grams of aniline were added, and the well-stoppered flask allowed to stand in ice-water for twelve hours. At the end of this time 3.5 grams of a solid, which proved to be acetanilide, had crystallized out.

[1] But a very small amount of benzoic acid is produced. This proves that under these conditions but little benzoyl acetyl oxide is formed, for this substance is hydrolyzed by moist air, and the resulting benzoic acid would appear in the alkaline solution.

[2] Ber. d. chem. Ges., 33, 1574.

The ether was filtered off and evaporated to one-third its bulk, in the cold, and 250 cc. of ligroin were then added. There separated 10.5 grams of a red solid. This was extracted with sodium carbonate solution, which was then acidified, giving a crystalline precipitate of benzoic acid. The remainder was boiled with water until no more dissolved and the water decanted from a dark-red, insoluble oil. The substance crystallizing from the water was acetanilide. The dark-red oil, when recrystallized from ligroin, melted at 34° to 35° and was azoxybenzene.

The ligroin-ether solution was evaporated *in vacuo* in the cold, and the remainder extracted with low-boiling petroleum ether (40°), and the ether evaporated. The remainder had the penetrating odor of benzoyl hydrogen peroxide. It was taken up in ice-cold caustic soda, leaving a residue of benzoyl peroxide, which was filtered. The cold caustic soda solution was then precipitated with barium chloride, yielding a small quantity of a precipitate which decomposed on standing over night at 0°. It was probably benzoperacid. All of the crude acetanilide which separated gave a sharp odor of phenylisonitrile on warming with alkalies pointing to the intermediate formation of phenylhydroxylamine, but not enough of this substance was present to be isolated. In all there were obtained in a pure state 9.3 grams acetanilide, 4.7 grams benzoic acid, 2.5 grams azoxybenzene, 0.5 gram benzoyl peroxide, and traces of benzoperacid. In another experiment in which we used one-half as much peroxide, we were able to isolate 3 grams of aniline benzoate also, with the other products the same, except that no benzoperacid could be detected. The first change in this reaction, which is very gradual, is always the separation of acetanilide, and no oxidation takes place until this change has begun. This fact proves conclusively that the benzoyl acetyl peroxide is not in itself capable of oxidizing aniline, but that it must first be separated into benzoperacid and acetanilide before its oxidizing action can become apparent. The benzoperacid then changes the aniline to azoxybenzene, probably with the intermediate formation of phenylhydroxylamine, while it is itself converted to benzoic acid. If an excess of peroxide is present, then some benzo-

peracid can be isolated. At the end of the reaction, if an excess of aniline is used, then aniline benzoate appears.

Pure benzoyl acetyl peroxide does not produce any marked effect on hydroquinone in benzene for forty-eight hours, if water is excluded; after this time oxidation gradually sets in with the production of quinhydrone. That a change finally sets in is probably due to the fact that a minute quantity of water, which cannot be excluded in sealing up a flask, gradually causes hydrolysis with the formation of benzoperacid, while the latter oxidizes the hydroquinone to quinhydrone and water, so that the reaction, once begun, would go on with increasing velocity.

Although pure benzoyl acetyl peroxide is not capable of oxidizing action, the aqueous solutions are, for they promptly liberate iodine from potassium iodide. This difference between the normal solid and the solution is due to hydrolysis. This change was followed out quantitatively in the following manner:

Ten flasks, with necks drawn out for sealing, were filled with 2 grams each of benzoyl acetyl peroxide and 100 cc. of water. The containers were then filled and placed in a shaker kept at 26° in a thermostat. The flasks were opened in the order given in the following table, the contents filtered, and the active oxygen in solution determined by means of acid potassium iodide and titration with N/20 sodium thiosulphate. In a certain number of flasks the solid residue was weighed to determine the point at which equilibrium, if any, was reached:

Hours.	Thiosulphate.	Active oxygen in solution.	Benzoyl acetyl peroxide represented.	Solid left.	Active oxygen in solid.	Total active oxygen.
18	44.098	0.0353	0.3967			
24	50.125	0.041	0.4611	1.49		
30	71.335	0.057	0.642			
48	84.04	0.067	0.756	1.31		
72	135.0	0.108	1.22	0.91		
96	147.34	0.118	1.326			
120	149.41	0.1195	1.345			
144	156.25	0.125	1.407	0.7011[2]	0.0464	0.1714
216	155.6	0.1245	1.326	0.7166[2]	0.0469	0.1715
404	138.9[1]	0.1112	1.259	0.7467[2]	0.0494	0.1606

[1] Slight pressure in tube on opening.
[2] Pure benzoyl peroxide.

Calculated total active oxygen in 2 grams of benzoyl acetyl peroxide, 0.1778.

The solid, after twenty-four hours, melted for the most part at 39° to 40°, only a small portion having a higher melting-point, the amount of benzoyl peroxide gradually increased until, after one hundred and forty-four hours it melted at 106° to 107° sharp, and was pure benzoyl peroxide. Before this time the residual solid was a mixture of benzoyl peroxide and unchanged benzoyl acetyl peroxide, so that, as the relative proportions were unknown, it was impossible to calculate the amount of active oxygen remaining. After all had been converted to benzoyl peroxide, as was the case in the last three experiments, it was possible to calculate the active oxygen remaining in the solid and add it to that found in titrating the solution, and the sum of these two quantities determines whether active oxygen is lost during the hydrolysis. As will be seen from the last column, no such loss took place until four hundred and eight hours were reached, when the tube showed slight pressure on opening. The total quantity of active oxygen present in the benzoyl acetyl peroxide therefore remains after the hydrolysis.

Benzoyl acetyl peroxide, at room temperatures, is slowly attacked by normal caustic soda or caustic potash, giving off oxygen and depositing benzoyl peroxide, which latter is quite stable in the cold, a fact which was also observed by Nef.[1] Baeyer demonstrated that the acid sodium salt of benzoperacid also rapidly gives off oxygen and leaves sodium benzoate and benzoyl peroxide,[2] and to explain this change he assumes that 3 molecules of benzoperacid form one of benzoyl peroxide and one of an oxygenated benzoperacid, which latter then decomposes into oxygen and benzoic acid:

$$\left.\begin{matrix} C_6H_5CO.O.OH \\ C_6H_5CO.O \\ C_6H_5CO.O \end{matrix}\right\} .OH = C_6H_5CO.O.O.COC_6H_5 + C_6H_5CO.O.O.O.H + H_2O.$$

If this same reaction were to take place in aqueous solution, then, as there is no loss of oxygen in the above experiments,

[1] Ann. Chem. (Liebig), **298**, 285.

[2] Ber. d. chem. Ges., **33**, 1570.

we would have to assume that the oxygenated benzoperacid is stable except in the presence of alkalies, and that the primary result is the hydrolysis of benzoyl acetyl peroxide to benzoperacid and acetic acid. It will be shown that this is not correct.

If Baeyer's equation is correct, then the 2 grams of benzoyl acetyl peroxide hydrolyzed above should, when equilibrium is reached, leave 0.89 gram of benzoyl peroxide as an insoluble remainder, and the solution should contain 0.1143 gram of active oxygen. However, as will be seen from the table, the complete change to benzoyl peroxide, when all benzoyl acetyl peroxide has disappeared, results after one hundred and forty-four hours, and then leaves only 0.7 gram, approximately, of benzoyl peroxide, and 0.125 gram active oxygen in solution. This would more nearly represent a change in which one-fourth the active oxygen had separated as benzoyl peroxide.

Another view of this change was, *a priori*, not unreasonable, namely, that benzoyl acetyl peroxide suffers gaseous dissociation into the anions of benzoic and acetic acids,

$$C_6H_5CO.OO.COCH_3 = C_6H_5\overline{C}O.O + CH_3\overline{C}O.O,$$

and that the two benzoic acid ions then unite to form the insoluble benzoperoxide, leaving the acetic acid anions as the active constituent. This view is not tenable, however, because:

1. The amount of benzoyl peroxide formed would then contain one-half the active oxygen. Two grams of benzoyl acetyl peroxide in the above experiment should yield, if all the benzoyl was converted into benzoyl peroxide, 1.344 grams of the latter instead of 0.75 gram as found.

2. Benzoyl peroxide is produced from the clear solution, after filtering.

3. Dilute solutions of benzoyl acetyl peroxide in absolute ether or petroleum ether, even after standing thirteen days, deposited unchanged peroxide on evaporation.

4. The molecular weight determination in benzene, even at great dilution, gave numbers so near the theoretical that no

conclusion as to dissociation could be drawn. Found, M 169; calculated, M 180. This difference is no greater than was found to be true for naphthalene in solution in the same benzene and at the same concentration.

The explanation which we have to offer for the changes which occur in solutions of benzoyl acetyl peroxide is briefly as follows:

The hydrolysis of benzoyl acetyl peroxide occurs in two directions, resulting in the formation of benzoperacid and acetic acid on the one hand, and acetoperacid and benzoic acid on the other. These changes can be represented by the equations:

(1) $C_6H_5CO.O.O.COCH_3 + HOH = C_6H_5CO.O.O.H + CH_3.CO.OH$;

(2) $C_6H_5CO.O.O.COCH_3 + HOH = C_6H_5CO.OH + CH_3.CO.O.O.H$.

From recent investigations made for us by Mr. Clover it appears that the hydrolysis represented in equation (2) takes place more readily than that represented in equation (1). Moreover, the secondary reaction resulting in the formation of benzoyl peroxide is due to the action of benzoperacid formed in (1) upon the still unchanged benzoyl acetyl peroxide. Thus:

(3) $C_6H_5CO.O.O.COCH_3 + C_6H_5CO.O.O.H = C_6H_5CO.O.O.COC_6H_5 + CH_3.CO.O.O.H$.

It is to be assumed that of four molecules of benzoyl acetyl peroxide which pass into solution, one remains unchanged, one is hydrolyzed according to equation (1), and two are hydrolyzed according to equation (2), it follows that the resulting benzoyl peroxide as formed in (3) will contain one-fourth the active oxygen present. This, it will be noted, corresponds to the amount actually found by experiment, the details of which are given in the preceding table.

The hydrolyzed solution of benzoyl acetyl peroxide, therefore, yields an insoluble precipitate of benzoyl peroxide and a clear liquid which contains acetic and benzoic acids, some benzoperacid, and chiefly acetoperacid. The presence of ben-

zoic acid is indicated by its crystallization from cooled, concentrated hydrolyzed solutions. Attempts to produce benzoyl peroxide by the action of benzoic acid upon benzoperacid gave negative results.

The amount of benzoperacid in the fully hydrolyzed solution will vary with the condition of hydrolysis. Obviously, if the reaction (3) is retarded it will result in the formation of an excess of benzoperacid over and above what is necessary to combine with the unhydrolyzed peroxide. Under such conditions the solution may contain 10 to 20 per cent of the active oxygen in the form of benzoperacid. On the other hand, conditions which hasten reaction (3) yield solutions containing little or no benzoperacid. It is evident, therefore, that the chemically and bacterially active constituent in the hydrolyzed solution of benzoyl acetyl peroxide is acetoperacid, either alone or associated with small but variable amounts of benzoperacid.

The use of solutions of benzoyl acetyl peroxide as germicides rendered a determination of the solubility in water necessary. The best method of arriving at accurate results was to decompose the substance with N/20 potassium hydroxide, and to titrate the excess of alkali with N/20 hydrochloric acid. If a weighed quantity of benzoyl acetyl peroxide is treated with an excess of N/20 potassium hydroxide, and at once warmed on a water-bath until all benzoyl peroxide has disappeared, the results invariably show the neutralization of more than the calculated quantity of caustic potash by 1 or 2 per cent. If, on the other hand, the peroxide is allowed to stand in the cold with the alkali for twenty-four hours, until the benzoyl acetyl peroxide is completely converted to benzoyl peroxide, and the solution is then warmed on the water-bath, the results are very accurate and correspond exactly to those calculated for the production of 2 molecules of acid.

0.2263 gram substance treated with 70 cc. N/20 potassium hydroxide required 10.9 cc. N/20 hydrochloric acid to neutralize. Calculated, 10.9 cc.

0.2518 gram substance treated with 70 cc. N/20 potassium hydroxide required 14.3 cc. N/20 hydrochloric acid to neutralize. Calculated, 14.1 cc.

Having established the accuracy of the method, we carried out the following experiments:

The peroxide, purified by several recrystallizations, was finely pulverized and then shaken with water at 25°. The amount of peroxide used did not affect the results, but the time of shaking did. It was necessary to shake for two or three minutes until a maximum solubility was reached. The increase in the amount in solution with length of shaking is due to the changes shown in the table given above, and, as indicated, the rise is a slow one. Changes of temperature, of course, materially affect the result.

Three-tenths gram substance was shaken with 110 cc. water, at 25°, filtered quickly through asbestos with suction, and 50 cc. removed and treated with 10 cc. N/20 caustic potash. After warming on the water-bath for several hours the excess of caustic soda was titrated.

	Time. Minutes.	Caustic potash required.	N/20 thiosulphate used to determine active oxygen.
1	5	7.2	7.0
2	10	7.3	7.3
3	15	7.4	7.4
4	20	7.5	7.5
5	30	7.7	7.7
6	40	8.2	8.2

The above table shows that for 1 molecule of peroxide in solution there is 1 atom of active oxygen, for the number of cubic centimeters of N/20 caustic potash and N/20 thiosulphate are the same, and 2 molecules of caustic potash in forming 2 molecules of salt from 1 of peroxide are equivalent to 2 molecules of thiosulphate in reducing iodine. This fact confirms the view that the first change is hydrolysis with the production of peracids,[1] as indicated above in equations 1 and 2.

The solubility, after five minutes, is therefore the equivalent of 7.1 cc. caustic potash ± 1 per cent, which corresponds to 0.639 gram per liter. This would represent 0.0568 gram active oxygen per liter. A 1 per cent hydrogen peroxide solution would contain 4.7 grams active oxygen per liter, or

[1] Electric conductivity measurements of solutions of benzoyl acetyl peroxide showed that rapid hydrolysis takes place. With 20,000 ohms' resistance the bridge readings fell from 850 to 340 in twelve minutes.

eighty times as much. Nevertheless, as will be shown below, these dilute solutions of benzoyl peroxide have a much greater germicidal action than even moderately concentrated ones of hydrogen peroxide. The reason for this is, *a priori*, not apparent, for in the one case we have a substance of the formula H.O.O.H and in the other $C_6H_5CO.O.O.H$. The germicidal action is, therefore, not due exclusively to the absolute quantity of active oxygen in unit space, so that some other cause, of which we cannot at present furnish an explanation, must be at the bottom of this remarkable fact. Hydroperoxide, when pure, is practically odorless, benzoperacid and acetoperacid, both of which have the same intense germicidal action, have most penetrating odors, resembling hypochlorous acid. This latter fact suggests a study of hypochlorous acid from the standpoint of a peroxide, HCl.O.O.ClH. All of these facts point to a difference between hydroperoxide and the organic acid peroxides which are germicides, which must be a subject of future investigation.

The decomposition of benzoyl acetyl peroxide with sodium ethylate gives benzoperacid and, apparently, no acetoperacid. Seven and a half grams of pure benzoyl acetyl peroxide were dissolved in 200 cc. absolute ether and cooled to —12°. 0.94 gram of sodium dissolved in alcohol and cooled to —12° was then slowly added, care being taken to allow no rise in temperature. The solution instantly forms a precipitate which almost solidifies the entire mass. The precipitate was allowed to stand for ten minutes, during which time it gave off some oxygen. Two hundred grams of ice were then added and shaken until all the solid went into solution. The ether was then separated and the remainder, after adding frozen dilute sulphuric acid, was extracted five times with ethyl chloride. On evaporating the ethyl chloride, a solid remained having the intense odor of benzoyl peroxide. This, when treated with sulphuric acid and alcohol, yielded only benzoic ester, and no acetic ester. The solid is, therefore, a mixture of benzoperacid and benzoic acid. It may be possible, by special methods, to isolate acetoperacid.

ACETYL PEROXIDE.

Acetyl peroxide is best prepared as follows: Commercial

barium dioxide is covered with water, cooled in a freezing-mixture, and then acetic anhydride and dilute hydrochloric acid are added alternately in small quantities, with frequent shaking, until all barium dioxide is used up. Care must be taken not to have the liquid alkaline during the reaction. The mixture is finally acidified with hydrochloric acid, which facilitates the separation of acetyl peroxide, and the crystals of the latter body are filtered off, dried, and recrystallized from ligroin.

Seven and one-tenth grams acetyl peroxide were dissolved in 50 cc. of absolute ether and then 1.38 grams of sodium dissolved in the smallest amount of alcohol slowly added, the whole being well shaken and cooled to —20°. The pasty mass was then poured into 2 volumes of cold petroleum ether and filtered on a Brühl filter. When allowed to stand *in vacuo*, a white salt remains which explodes violently when brought into a flame. The salt dissolves in water, but instantly begins to give off oxygen. On acidifying with frozen dilute sulphuric acid, an oil was produced with a most intense odor of oxide of chlorine, which is characteristic of the peracids. The oil was extracted with ethyl chloride and the latter evaporated. A small quantity of oil, with an indescribably intense odor, remained, but it was so volatile that in a few minutes all was gone. This substance is undoubtedly acetoperacid, but it decomposes so rapidly that its isolation in a pure state will be very difficult. Several attempts to obtain larger quantities gave the same result. The explosive sodium salt, mentioned above, soon loses its character, even when placed in a desiccator.

Unlike benzoyl acetyl peroxide, acetyl peroxide, on standing with water, gradually gives off oxygen. Five grams in 50 cc. of water evolved oxygen during one month, and at the end of that period still contained active oxygen. A solution of acetyl peroxide, 1.2 grams in 50 cc. of water, gave the theoretical amount (0.166 gram) of active oxygen on titration, even after standing but a few minutes, so that hydrolysis was practically complete. After seventeen days, however, this active oxygen had fallen to 0.03 gram.

GERMICIDAL ACTION.[1]

It has been pointed out that certain peroxides are chemically indifferent while others are active oxidizing agents. The chemical behavior in this respect offers a very good indication of the action of these bodies upon bacteria. Those peroxides which are chemically inert are also germicidally inactive, and *vice versa*. Before proceeding into a detailed consideration of this aspect, it may be well to obtain a general view, as it were, of the peroxides heretofore mentioned.

Hydroperoxide, H.O.O.H ;

Benzoyl peroxide, $C_6H_5CO.O.O.COC_6H_5$;

Acetyl peroxide, $CH_3CO.O.O.COCH_3$;

Benzoyl acetyl peroxide, $C_6H_5CO.O.O.COCH_3$.

It will be seen from the above formulas that the three organic compounds possess a symmetrical structure similar to that of ordinary hydrogen peroxide. The latter substance, as is well known, is a fair germicidal agent, especially when strong solutions are employed. On the other hand, benzoyl peroxide is difficultly soluble, does not undergo hydrolysis, has no oxidizing action, and is wholly without effect upon bacteria. When compared with acetyl peroxide and benzoyl acetyl peroxide, however, a remarkable difference is observed. The last two compounds may also be looked upon as chemically and biologically inert, but, unlike benzoyl peroxide, they readily undergo hydrolysis with the production of intense oxidizing and actively germicidal bodies. The hydrolysis of these bodies has already been discussed, and it is sufficient in this connection to indicate that the active peroxides resulting from the hydrolysis of the inactive forms are :

Benzoperacid, $C_6H_5CO.O.OH$;

and Acetoperacid, $CH_3CO.O.OH$.

These peracids possess, it will be noted, an asymmetrical structure, and, as stated above, they are extremely active not only chemically but also germicidally. In fact, when solutions of these peroxides are tested upon bacteria and the effect

[1] The bacteriological work *in extenso* will appear in the *Journal of Experimental Medicine*, 1902.

produced is compared with that caused by a solution of hydrogen peroxide of like oxygen content, that is, of equimolecular strength, it will be found that these organic peroxides are at least several hundred times more active than hydrogen peroxide. Inasmuch as the active oxygen contents in such solutions is the same, it is difficult to explain the difference in effects by mere reference, as has been the case heretofore, to nascent oxygen. Either the active oxygen does not directly participate in the reaction, or else we must assume that it is liberated from the organic peroxides with an enormously higher potential energy than is the case in hydrogen peroxide. It should be noted in passing that while hydrogen peroxide loses its available oxygen readily and even violently, on contact with enzymes, blood and other organic fluids, no such rapid disengagement is observable with the peracids. Indeed, the addition of benzoyl acetyl peroxide to blood, while it causes in time the destruction of hemoglobin, yet it does so without visible evolution of gas.

The simplest explanation of the difference in action between the peracids and hydrogen peroxide appears to us to be based upon the behavior of the acid ions. The acetyl and benzoyl ions, just as the sulphuryl ion in Caro's acid, are to be considered as the active groups which, by their avidity for proteids and other chemical substances, induce the pronounced germicidal and oxidizing effects.

The activity of the hydrolyzed solution of diacetyl peroxide is due to acetoperacid, while that of benzoyl acetyl peroxide is due at times wholly to acetoperacid, more often, however, to this peracid plus variable amounts of benzoperacid as has already been explained.

Benzoyl peroxide may be dismissed in a few words. Since it does not hydrolyze it does not exert any germicidal action whatever. This is most clearly seen by the fact that the extremely weak cholera vibrio is wholly unaffected by benzoyl peroxide.

The hydrolyzed solutions of acetoperoxide and benzoyl acetyl peroxide by contrast exhibit remarkable germicidal effects. Thus, solutions containing 0.01, and even 0.005, per cent active oxygen are capable of destroying within a minute

all known disease-producing bacteria, including the spores of such extremely resistant forms as the potato bacillus.

The methods of testing these solutions need not be considered here, inasmuch as they are given in detail in the paper referred to. It will not be out of place, however, to present a few tabulated experiments which will serve to show at a glance the results obtained. In these tables + indicates that a growth resulted, in other words, that disinfection did not occur. On the other hand, — indicates that no growth occurred and hence the germicidal action is manifested. It should be stated, also, that control experiments were invariably made to test the viability of the cultures used for each experiment.

Table I.

Hydrolyzed Acetyl Peroxide (1–600), 0.0226 per cent active oxygen.

	Minutes.						
	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—
Strept. pyogenes	—	—	—	—	—	—	—
Spores anthrax B.	+	—	—	—	—	—	—
" hay B.	+	—	—	—	—	—	—
" potato B.	+	—	—	—	—	—	—

The acetyl peroxide for this experiment was prepared according to the method previously given. It will be seen from the above table that the relatively weak solution possesses energetic germicidal powers. Even a weaker solution will produce practically the same results, which, in that case, are comparable with those given in Tables II. and III.

A comparison with Table IV. will show that a hydrogen peroxide solution containing twice the amount of active oxygen is, nevertheless, a very feeble germicide. Indeed, to produce like results, it would be necessary to use a hydrogen peroxide solution containing 100 to 200 times as much active oxygen as that contained in the peracid solution. Table IV.

also shows the action of a 5 per cent carbolic acid solution on spores, which stands out in marked contrast to the action of the several peroxides.

Table II.

Hydrolyzed Benzoyl Acetyl Peroxide.

	(1–177), 0.05 per cent active oxygen. Minutes.							(1–2940), 0.003 per cent active oxygen. Minutes.						
	1.	3.	5.	10.	15.	30.	60.	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—	+	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—	+	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Strept. pyogenes	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Spores anthrax B.	—	—	—	—	—	—	—	+	+	+	+	+	—	—
" hay B.	—	—	—	—	—	—	—	—	—	—	—	—	—	—
" potato B.	—	—	—	—	—	—	—	+	+	+	+	+	+	+

In Table II. are given the results obtained with strong and dilute hydrolyzed solutions of benzoyl acetyl peroxide. While the strong solution kills everything almost instantly, the weaker solution (1–3000) destroys the vegetating germs, as a rule, within one minute, but, as might be expected, the spores require an appreciable time.

Table III.

Benzoperacid (1 : 2500), 0.0046 per cent active oxygen.

	Minutes.						
	1.	3.	5.	10.	15.	30.	60.
B. pyocyaneus	—	—	—	—	—	—	—
B. coli	—	—	—	—	—	—	—
B. typhosus	—	—	—	—	—	—	—
B. diphtheriæ	—	—	—	—	—	—	—
Vib. choleræ	—	—	—	—	—	—	—
S. pyog. aureus	—	—	—	—	—	—	—
Strept. pyogenes	+	—	—	—	—	—	—
Spores anthrax B.	+	+	—	—	—	—	—
" hay B.	—	—	—	—	—	—	—
" potato B.	+	—	—	—	—	—	—

The benzoperacid used for the above experiment was prepared in a pure form by the hydrolysis of benzoyl acetyl peroxide by means of sodium ethylate. The result, it will be

seen, is in accord with those given by the hydrolyzed solutions of acetyl peroxide and benzoyl acetyl peroxide.

Table IV.

	Hydrogen Peroxide, (1–1000). 0.05 per cent active oxygen. Minutes.							Phenol. 5 per cent. Minutes.				
	1.	3.	5.	10.	15.	30.	60.	1.	5.	15.	30.	60.
B. pyocyaneus	+	+	+	+	+	—	—	—	—	—	—	—
B. coli	+	+	+	+	+	+	+					
B. typhosus	+	+	+	+	+	+	+	—	—	—	—	—
B. diphtheriæ	+	+	+	+	+	+	+					
Vib. choleræ	+	—	—	—	—	—	—					
S. pyog. aureus	+	+	+	+	+	+	+					
Strept. pyogenes	+	+	+	+	+	—	—					
Spores anthrax B.	+	+	+	+	+	+	+	+	+	+	+	+
" hay B.	+	+	+	—	—	—	—	+	+	+	+	+
" potato B.	+	+	+	+	+	+	+	+	+	+	+	+

The results recorded in Table IV. serve for comparison with those given in the preceding table. Thus, it will be seen that while the hydrogen peroxide solution contains ten times as much active oxygen as the benzoperacid solution used in Table III., the germicidal effect is entirely different.

These few examples serve to illustrate the interesting fact which we have brought out, namely, that while the symmetrical organic peroxides are inert, the asymmetrical peracids easily rank among the most powerful germicidal agents known. For a more extended account of these bodies it will be necessary to refer the reader to the paper which deals especially with their germicidal behavior.

The results given in this paper are by no means complete, but as one of us expects to be away from his work for a year or more, we thought it best to publish the results obtained up to this time. The work in this interesting and large field will be continued in the future and, as we hope, many of the doubtful points cleared up. The bacteriological work will also be continued with this and other bodies of the same class.

LABORATORIES OF GENERAL CHEMISTRY AND OF HYGIENE, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICH.

Contributions from the Chemical Laboratory of Harvard College.

CXXIX.—ON δ-NITROPYROMUCIC ACID.[1]

By Henry B. Hill and George R. White.

In 1888 Hill and Palmer[2] found that δ-sulphopyromucic acid was decomposed by concentrated nitric acid with the formation of the δ-nitropyromucic acid which had been obtained by Klinkhardt[3] a few years previously by the action of nitric acid upon dehydromucic acid. They also found that a neutral body was formed at the same time, which appeared to be a dinitrofurfuran, but the material at their disposal did not enable them to study it in detail. From the β-brom-δ-sulpho- and the β,γ-dibrom-δ-sulphopyromucic acids they obtained the corresponding bromine derivatives of the δ-nitropyromucic acid, and they further isolated the β,β-dibrom-α,α-dinitrofurfuran. Similar acids were obtained a few years later by Hill and L. L. Jackson,[4] and by Hill and Hendrixson[5] from the chlorsulphopyromucic acids.

It seemed to us that the material needed for an extended study of the δ-nitropyromucic acid could be made most conveniently from δ-sulphopyromucic acid, since the methods which were then known for the preparation of dehydromucic acid involved a great expenditure of time and labor. Most of the nitropyromucic acid which we have used was made in this way, but convenient methods have recently been described[6] for making dehydromucic acid in large quantities, and the method of Klinkhardt is now much more economical. Our study of the nitropyromucic acid was not far advanced when it was interrupted by the removal of one of us from Cambridge, and its progress has since been delayed by circumstances beyond our control. Since further collaboration seems to be out of the question, we have thought it best to

[1] The work described in the following paper formed a part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, in May, 1896, by George Rantoul White, candidate for the degree of Doctor of Philosophy.

[2] This Journal, **10**, 380; Proc. Am. Acad., **23**, 195.

[3] J. prakt. Chem., [2], **28**, 51.

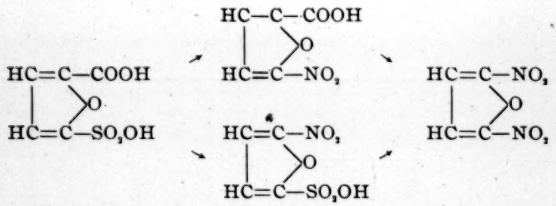
[4] This Journal, **12**, 126; Proc. Am. Acad., **24**, 361.

[5] This Journal, **15**, 149; Proc. Am. Acad., **25**, 283.

[6] Hill: Ber. d. chem. Ges., **32**, 1221; Phelps and Hale: This Journal, **28**, 45; Yoder and Tollens: Ber. d. chem. Ges., **34**, 3446.

publish in their present incomplete form the results which we have obtained.

Concentrated nitric acid acts upon δ-sulphopyromucic acid at ordinary temperatures and the reaction is completed on gentle warming. The reaction proceeds simultaneously in two directions, but we have been unable to determine the conditions favorable to the formation of either product. Nitropyromucic acid is formed by the replacement of the sulpho group, and at the same time a nitrofurfuransulphonic acid results from a similar replacement of the carboxyl. The former is sparingly soluble in cold water, while the latter can be isolated through its sparingly soluble potassium salt. Both of these bodies are then converted into dinitrofurfuran by the continued action of fuming nitric acid, although the nitropyromucic acid is but slowly attacked unless sulphuric acid is present in considerable quantity.



When dehydromucic acid is treated with 10 parts of nitric acid and 1 part of sulphuric acid, as recommended by Klinkhardt, but little dinitrofurfuran is formed.

We have also found that nitropyromucic acid may be made by the action of nitric acid upon a solution of pyromucic acid in fuming sulphuric acid without isolating the sulphonic acid. A saving in time and labor is thus effected, but great care must be taken to avoid any considerable rise in temperature and consequent destructive oxidation.

Nitropyromucic acid forms stable salts, but it is rapidly decomposed by an excess of an alkaline hydrate. With baric hydrate three equivalents were found to be involved in the reaction, baric nitrite being formed, and at the same time a

deep-brown, insoluble barium salt, the nature of which we have not yet determined. Dinitrofurfuran is readily attacked by baric hydrate with the formation of baric nitrite and baric maleate. The reaction is, however, complicated, since the yield of these two salts is but little more than one-half of the theoretical amount, and decidedly less than three equivalents of baric hydrate are used in the reaction. At the same time small amounts of baric carbonate and ammonia are formed. Nitrofurfuransulphonic acid is also decomposed in a similar way in alkaline solution.

We have studied with care two colored bodies which are formed under certain conditions by the action of aniline upon nitropyromucic acid, but we have not yet reached definite conclusions as to their structure. If aniline hydrochloride is added to nitropyromucic acid dissolved in a solution of sodic acetate, reaction soon sets in and a red, insoluble substance is slowly thrown down with the evolution of carbon dioxide. The crude product contains chiefly a yellow body, the formula of which is $C_{16}H_{13}N_3O$, but mixed with a small amount of another substance with the formula $C_{17}H_{13}N_3O_3$. These bodies are evidently formed according to the equations:

$$C_5H_3NO_5 + 2C_6H_7N = C_{16}H_{13}N_3O + 2H_2O + CO_2;$$
$$C_5H_3NO_5 + 2C_6H_7N = C_{17}H_{13}N_3O_3 + 2H_2O.$$

The yellow substance $C_{16}H_{13}N_3O$, which is the main product, is a neutral, indifferent body; it gives the color reaction of Bülow[1] characteristic for the phenylhydrazones, and yields, when reduced with zinc and acetic acid, ammonia, aniline, and succinanil. These facts seem to warrant the conclusion that the nitro group has been directly involved in the formation of a phenylhydrazone, but further experiments must determine whether the body still contains the furfuran ring intact, or whether its oxygen has already been replaced by the phenylimido group. We have not yet been able to establish experimentally the connection between this body and the crimson substance which contains an additional CO_2. Similar derivatives of paratoluidine were also made.

[1] Ann. Chem. (Liebig), **236**, 195; Cf. V. Meyer: *Ibid.*, **264**, 130; Fischer: Ber. d. chem. Ges., **23**, 384.

Action of Nitric Acid upon δ-Sulphopyromucic Acid.

The δ-sulphopyromucic acid was prepared by exact precipitation of a solution of its barium salt with sulphuric acid. The filtered solution was concentrated on the water-bath, and the acid then thoroughly dried in a desiccator over sulphuric acid. The finely powdered acid was then slowly added with constant stirring to three times its weight of concentrated nitric acid, the specific gravity of which was at least 1.50, carefully cooled with ice. The solution was allowed to stand over night at ordinary temperature, then warmed for a short time, and a part of the nitric acid driven off at a gentle heat. The crystalline mass which was obtained on cooling was treated with a small amount of cold water, drained well with the pump, and washed with a little cold water. This crystalline product is δ-nitropyromucic acid mixed with varying amounts of dinitrofurfuran, while the aqueous solution contains nitrofurfuransulphonic acid. Although nitropyromucic acid and dinitrofurfuran may be separated partially by the use of solvents, we have usually preferred to neutralize the nitropyromucic acid in dilute solution with sodic carbonate, and to remove the dinitrofurfuran completely by extracting the feebly alkaline solution with ether. The nitropyromucic acid is then extracted from the acidified solution with ether and further purified by recrystallization from hot water. The nitrofurfuransulphonic acid can easily be isolated from the acid mother-liquor by neutralizing it with potassic carbonate. The hot solution is a deep red-brown, and on cooling a highly colored potassium salt separates in abundance. The color may be removed by treatment with bone-black, and the potassic sulphate by recrystallization from hot water. A certain amount of the salt may be recovered from the mother-liquors by adding baric acetate in quantity sufficient to convert all the potassic sulphate into acetate and concentrating the filtered solution. The yield of these three products has varied greatly in successive preparations, and we have not been able to determine the precise cause of this variation. The maximum yield of each of the three products, necessarily in different preparations, was about 25 per cent of the sulphopyromucic acid

taken; ordinarily, however, the amounts obtained were much smaller.

The preparation of the dry δ-sulphopyromucic acid was a simple matter, but we thought that the time involved might be saved by allowing the nitric acid to act directly upon a solution of pyromucic acid in fuming sulphuric acid. At first we found great difficulty in maintaining a sufficiently low temperature, even in experiments conducted on a small scale, but by using a thin, seamless iron dish, set in a freezing-mixture, the reaction could easily be controlled. The iron dish was hardly attacked by the concentrated acids used. One part of pyromucic acid was dissolved in 3 parts of fuming sulphuric acid, the temperature not being allowed to rise above 20°. On the following day, 3 parts of fuming nitric acid of sp. gr. 1.51 were slowly added with constant stirring, the temperature being kept below 40° by means of a freezing-mixture. The product was kept in the freezing-mixture for at least an hour, and was then allowed to stand at ordinary temperature over night. The dinitrofurfuran and nitropyromucic acid were then extracted by ether from the diluted solution, and separated by means of a dilute solution of sodic carbonate, as before. By this method 100 grams pyromucic acid gave 17 grams of nitropyromucic acid and from 6 to 12 grams of dinitrofurfuran, but no nitrofurfuransulphonic acid could be isolated.

Nitrofurfuransulphonic Acid.

As yet we have succeeded in making the nitrofurfuransulphonic acid only by the action of nitric acid on the δ-sulphopyromucic acid, and we have not been able to prepare, from the sparingly soluble potassium salt by means of which we isolated it, any other salts by double decomposition.

Potassic Nitrofurfuransulphonate, $KC_4H_2NSO_6$.—This salt is very sparingly soluble in cold water, readily soluble in hot water, and as the solution cools it is deposited in brilliant, long, flat, rectangular prisms, which are anhydrous.

I. 0.6904 gram air-dried salt gave 0.2585 gram K_2SO_4.

II. 0.6182 gram air-dried salt gave 0.2320 gram K_2SO_4.

III. 0.4730 gram air-dried salt gave 26.2 cc. N over KOH at 27° and under a pressure of 764 mm.

	Calculated for $KC_4H_2NSO_6$.	Found. I.	II.	III.
K	16.92	16.82	16.85	....
N	6.07	....	....	6.20

When treated with twice its weight of concentrated nitric acid, the potassium salt yields dinitrofurfuran in abundance. On heating with distillable hydrobromic acid in a sealed tube, at 100°, it was completely decomposed. The diluted solution, when extracted with ether, yielded a crystalline acid which melted at 160° to 161°, after recrystallization from a small quantity of water, and contained the percentage of bromine required by a bromsuccinic acid.

0.2655 gram substance gave 0.2531 gram AgBr.

	Calculated for $C_4H_3BrO_4$.	Found.
Br	40.58	40.58

Qualitative tests showed that sulphuric acid had been formed, and at the same time the solution reduced cupric oxide vigorously in the cold. The body therefore appeared to have been decomposed according to the equation:

$$KC_4H_2NSO_6 + 3H_2O + HBr = C_4H_3BrO_4 + KHSO_4 + NH_3O.$$

α,α-Dinitrofurfuran.

All the material which we have used was made from pyromucic acid by the methods just described. Dinitrofurfuran is formed, however, in small quantity by the action of nitric acid upon dehydromucic acid, and the amount is apparently increased if sulphuric acid is also added. It may be made from nitropyromucic acid without difficulty by warming it to 60° with concentrated nitric acid to which an equal volume of sulphuric acid is added. The crude product which we obtained by extracting the alkaline solution of nitropyromucic acid with ether was recrystallized from hot alcohol.

I. 0.3250 gram substance gave 0.3603 gram CO_2 and 0.0520 gram H_2O.

II. 0.2793 gram substance gave 41.2 cc. N over KOH at 12°.5 and under a pressure of 780 mm.

	Calculated for $C_4H_2N_2O_5$.	Found. I.	Found. II.
C	30.38	30.24	....
H	1.28	1.79	....
N	17.76	....	17.95

α,α-Dinitrofurfuran is quite readily soluble in ether. It is sparingly soluble in cold alcohol, but dissolves freely on heating. It is readily soluble in benzol or in hot chloroform, but is almost insoluble in carbonic disulphide or ligroin. It dissolves sparingly even in boiling water, volatilizes slowly with steam, and crystallizes from hot aqueous solution in clustered needles. From alcohol it crystallizes in slender prisms which are not infrequently grouped together in feather forms. It is usually pale-yellow, but may be obtained nearly colorless by precipitating its solution in benzol with ligroin. It melts at 101°, and sublimes readily at a lower temperature.

Hill and Palmer noted that a filter-paper moistened with an alcoholic solution of dinitrofurfuran exposed to the vapors of ammonic sulphide was colored yellow at first, then salmon-red. The preliminary experiments which we tried with various reducing agents were so far from encouraging in their results that we have as yet made no more extended study of these products. We have, however, studied more in detail the decomposition which takes place in alkaline solution. Even in the cold, a yellow color is developed and a nitrite is formed; on heating, the reaction is completed in a short time.

A weighed amount of dinitrofurfuran was dissolved in about 200 times its weight of hot water and an excess of a titrated solution of baric hydrate was then added. A deep-red color was developed which immediately passed into a yellow, and this yellow color slowly faded on boiling. The clear solution gradually grew turbid and a small amount of ammonia was formed. The excess of baric hydrate was then precipitated by carbonic dioxide from the filtered solution, and the baric carbonate thus formed was dried and weighed. Two experiments, in each of which 0.790 gram of dinitrofurfuran was taken, showed that 1.34 and 1.30 molecules of baric hydrate had entered into reaction; the insoluble salt which had been thrown down in the boiling solution proved to be mainly baric carbonate, but the amount was insignificant, 0.25 and 0.27

molecule in the two cases. On concentrating the aqueous solution, a barium salt separated in flat, obliquely-truncated needles, which appeared to be identical in form and habit with baric maleate; in the mother-liquor was baric nitrite in abundance. The weights of the baric maleate obtained corresponded to 0.53 and 0.55 molecule respectively. The amount of nitrite formed was determined with separate portions of dinitrofurfuran, and as the mean of two determinations it was found that 62.5 per cent of the nitrogen had been converted into baric nitrite. The baric maleate was decomposed by dilute sulphuric acid, taking care to leave a trace of barium in solution, and the solid obtained by evaporation was then extracted with ether. The acid thus obtained was readily soluble in ether and very soluble in cold water. It melted at 131° to 132°, sublimed readily between watch-glasses, and the last portions of the sublimate melted at 52° to 53°. On evaporation with hydrochloric acid, a sparingly soluble acid was obtained which had all the characters of fumaric acid. In addition, the barium salt was shown to have the composition of baric maleate.

0.5946 gram air-dried salt lost, at 160°, 0.0405 gram H_2O.

	Calculated for $BaC_4H_2O_4.H_2O$.	Found.
H_2O	6.69	6.81

0.5421 gram salt, dried at 160°, gave 0.5024 gram $BaSO_4$.

	Calculated for $BaC_4H_2O_4$.	Found.
Ba	54.66	54.54

δ-Nitropyromucic Acid.

The nitropyromucic acid used was recrystallized from hot water, and agreed in properties with the description of Klinkhardt. In the preparation of salts of the acid we noticed that an excess of an alkaline hydrate immediately brought about a change of color, and that decomposition soon set in at ordinary temperatures. The change of color to a reddish-yellow is sufficiently well marked to serve as an indicator in the titration of the acid. In two successive trials 0.314 gram of the acid required 6.90 and 6.90 cc. of a baric hydrate solution, 1

cc. of which was equivalent to 2.88 cc. N/10 hydrochloric acid; the calculated amount is 6.94. With an excess of baric hydrate a dark-brown, flocculent precipitate is slowly formed at ordinary temperatures, and the same decomposition takes place at once on boiling; in either case exactly 1.5 molecules of baric hydrate are involved in the reaction. Baric nitrite is formed in abundance, but we have not succeeded in determining the nature of the insoluble product.

If ethereal solutions of nitropyromucic acid and aniline are mixed, aniline nitropyromucate at once separates in colorless, clustered leaflets. The salt is very sparingly soluble in ether or in cold alcohol, but it dissolves freely in boiling alcohol. On exposure to the air it rapidly turns dark in color. The salt dried in a desiccator gave the following results:

I. 0.2197 gram substance gave 0.4258 gram CO_2 and 0.0831 gram water.

II. 0.4427 gram substance gave 45.8 cc. N over KOH at 25° and under a pressure of 754 mm.

	Calculated for $C_{11}H_{10}N_2O_4$.	Found. I.	II.
C	52.76	52.86	....
H	4.03	4.23	....
N	11.23	....	11.53

This aniline salt is sparingly soluble in cold water and may be recrystallized from hot water. An aqueous solution at ordinary temperature is slowly decomposed with the precipitation of brownish flocks. If aniline is added to the aqueous solution, or better, aniline acetate, the reaction is accelerated, and a voluminous, brilliant-red precipitate is formed after the lapse of a few hours. This body may be prepared more conveniently by adding rather more than 2 molecules of aniline hydrochloride to nitropyromucic acid dissolved in a solution of sodic acetate. The solution should not contain more than 1.5 per cent of the nitropyromucic acid in order that no aniline salt may separate. The solution soon grows turbid and gradually deposits the red body; at the same time carbonic dioxide is slowly evolved. After standing for forty-eight hours at ordinary temperature the reaction is in great part completed, but the filtered solution again grows turbid and

continues for several days to deposit small amounts of the colored product. The reaction may be accelerated by heat, but the color of the product is then not so brilliant. The weight of the precipitate when dried was usually about 25 per cent more than that of the nitropyromucic acid taken. On closer examination the substance proved to be a mixture of two bodies which could easily be separated by means of chloroform. When thoroughly extracted with chloroform an orange-yellow body was left, which amounted to about 80 per cent of the mixture taken, while the dark-red chloroform solution contained a crimson substance.

The yellow body proved to be very sparingly soluble or insoluble in all ordinary solvents, except glacial acetic acid, in which it was not freely soluble even on boiling. As the solution cooled the body separated in nearly rectangular, four-pointed stars, which were deep-red in color but gave a yellow powder. The material thus purified gave the following results; in analyses IV. and VI. the substance was washed with alcohol and water:

I. 0.2201 gram substance gave 0.5855 gram CO_2 and 0.1004 gram H_2O.

II. 0.2152 gram substance gave 0.5725 gram CO_2 and 0.0974 gram H_2O.

III. 0.2215 gram substance gave 0.5892 gram CO_2 and 0.1019 gram H_2O.

IV. 0.2149 gram substance gave 0.5737 gram CO_2 and 0.0962 gram H_2O.

V. 0.4362 gram substance gave 58.9 cc. N over KOH at 15° and under a pressure of 769 mm.

VI. 0.4846 gram substance gave 65.8 cc. N over KOH at 17° and under a pressure of 773 mm.

	Calculated for $C_{16}H_{12}N_2O$.	Found.					
		I.	II.	III.	IV.	V.	VI.
C	72.95	72.57	72.57	72.54	72.83	....	....
H	4.98	5.10	5.06	5.14	5.01	....	....
N	16.01	....	....	....	....	16.03	16.08

When quickly heated the substance melted at 232°, but this melting-point was lowered several degrees by slow heating. The body was indifferent to aqueous acids or alkalies, but it

dissolved promptly in alcoholic soda or potassic hydrate with the formation of an intense carmine-red color; on dilution with water the original substance was apparently precipitated. It dissolves in concentrated sulphuric acid to form an orange-yellow solution. The addition of ferric chloride or potassic dichromate develops a deep greenish-blue color. The green tinge is apparently due to the yellow color of the sulphuric acid solution, or to an excess of the oxidizing agent. With ammonic sulphide in alcoholic solution a reduction-product is apparently formed which we have not further examined. Complete reduction is easily effected by the addition of zinc dust to the hot solution in somewhat diluted glacial acetic acid. After removing the zinc the solution gives, on concentration, long colorless needles which are sparingly soluble in cold water. The melting-point, 151° to 152°, and the behavior of the substance showed that it was succinanil, and its identity was established by analysis.

I. 0.2103 gram substance gave 0.5278 gram CO_2 and 0.0990 gram H_2O.

II. 0.3389 gram substance gave 24.1 cc. N over KOH at 20° and under a pressure of 761 mm.

	Calculated for $C_{10}H_9NO_2$.	Found. I.	II.
C	68.53	68.47	....
H	5.18	5.27	....
N	8.02	....	8.18

In the mother-liquor from the succinanil the presence of aniline and ammonia could easily be shown by qualitative tests.

The crimson body was obtained by distilling off most of the chloroform, adding alcohol to the residue, and washing the crystals which were thus separated with cold alcohol. For analysis it was recrystallized from glacial acetic acid, washed with water, and dried over sulphuric acid.

I. 0.1907 gram substance gave 0.4646 gram CO_2 and 0.0740 gram H_2O.

II. 0.3217 gram substance gave 37.4 cc. N over KOH at 16° and under a pressure of 773 mm.

	Calculated for $C_{11}H_{12}N_2O_3$.	Found. I.	Found. II.
C	66.40	66.45	....
H	4.26	4.34	....
N	13.71	....	13.82

This body is sparingly soluble in alcohol or ether, but is readily soluble in chloroform, benzol, or hot glacial acetic acid. From the latter solvent it crystallizes in flattened crimson needles, which melt at 218° when slowly heated, but decomposition apparently sets in at a lower temperature. We have not yet succeeded in preparing serviceable derivatives of this body.

We have also made the corresponding derivatives of paratoluidine. The properties of these bodies are almost identical with those of the aniline derivatives, and they were made and purified by the same methods. The yellow toluidine compound crystallized from glacial acetic acid in clustered prisms which melted at 250° when quickly heated.

I. 0.2226 gram substance gave 0.6053 gram CO_2 and 0.1188 gram H_2O.

II. 0.5060 gram substance gave 65.3 cc. N over KOH at 21° and under a pressure of 750 mm.

	Calculated for $C_{18}H_{17}N_3O$.	Found. I.	Found. II.
C	74.16	74.16	....
H	5.88	5.97	....
N	14.46	....	14.56

On reduction with concentrated acetic acid and zinc dust it gave ammonia, paratoluidine, and a body which melted at 153° to 154°, and had the percentage composition of a tolylsuccinimid.

I. 0.1844 gram substance gave 0.4712 gram CO_2 and 0.0984 gram H_2O.

II. 0.1773 gram substance gave 12.0 cc. N over KOH at 17° and under a pressure of 769 mm.

	Calculated for $C_{11}H_{11}NO_2$.	Found. I.	Found. II.
C	69.79	69.71	....
H	5.86	5.97	....
N	7.44	....	7.97

The crimson compound crystallized from glacial acetic acid in finely felted needles, which were decomposed on heating. When washed with water and dried over sulphuric acid it gave the following results:

I. 0.1651 gram substance gave 0.4124 gram CO_2 and 0.0810 gram H_2O.

II. 0.2233 gram substance gave 24.6 cc. N over KOH at 18° and under a pressure of 760 mm.

	Calculated for $C_{19}H_{17}N_3O_2$.	Found. I.	II.
C	68.01	68.13	....
H	5.11	5.49	....
N	12.57	....	12.77

THE QUANTITATIVE SEPARATION OF HYDROCHLORIC AND HYDROCYANIC ACIDS.

By Theodore William Richards and Sidney Kent Singer.

In the course of some recent work which involved the use of very pure potassic cyanide, the lack of a convenient method for determining the amount of chloride present in this salt became manifest. Accordingly, Miss Grace E. Dennett and Miss Selma Hunt, advanced students of chemistry at Radcliffe College, tested a new method, at the request of one of us. Unfortunately, lack of time prevented them from performing all the details necessary for the final judging of the method, but their results were so promising that the matter seemed worthy of further pursuit. This end we have accomplished, and the present paper contains a detailed description of the method.

In seeking to effect any separation, one naturally utilizes an operation which brings into play some property possessed by the two substances to be separated in as different a measure as possible. Now the most striking difference between hydrocyanic acid and hydrochloric acid is the difference in the degree of their ionization. According to Walker and Cormack[1] the "dissociation constant" of a tenth-normal solution of hydrochloric acid is about nine thousand times as great as that of equally concentrated hydrocyanic acid. Both undissociated

[1] J. Chem. Soc., London, 77, 5 (1900).

acids are very volatile, hydrochloric acid being the more so, but ions have little or no tendency to leave an aqueous solution with steam. Hence it seemed possible that by evaporating a dilute solution of the mixed acids, with continual addition of water, all the hydrocyanic acid might be expelled without the loss of an important amount of hydrochloric acid.

Since some experiments of Richards and Mallinckrodt, as yet unpublished, showed that a tenth-normal solution of hydrochloric acid emits only a negligible amount of hydrochloric acid with its vapor, the solutions were kept at this dilution by the frequent addition of water. The evaporation was effected in vessels of various shapes, all of which gave fairly satisfactory results. The chief disadvantage of an open dish on the steam-bath was the danger of absorbing hydrochloric acid from the air of the crowded laboratory during the protracted evaporation, and the chief disadvantage of a common flask, or of a large beaker with a funnel over it, was the danger of loss of liquid in the minute drops caused by rapid ebullition. We finally decided upon the use of a common untubulated retort of 500 cc. capacity, with its neck directed upwards at an angle of 45°. In this vessel all the analyses given below, except Nos. 5, 6, and 15, were boiled. A large beaker with an inverted funnel over it was used in the three cases named as exceptions. In every case the precipitation was effected in a large beaker.

Experiments with perfectly pure hydrocyanic acid showed that two hours' boiling was enough to expel every perceptible trace of the acid. The cooled solution gave no cloudiness with argentic nitrate.

In the next place a series of experiments was executed with "C. P." potassic cyanide of commerce as the starting-point. A large volume of solution was made up, and for each analysis a quantity containing 1.25 grams of the salt was taken. This material was diluted to the bulk of about 400 cc., and to it were added 5 cc. of sulphuric acid. The mixture was submitted to active ebullition, with the addition of water in such measure as to prevent the volume from ever falling below 300 cc. At the end of a prearranged time the ebullition was stopped and the remaining chloride was precipitated with argen-

tic nitrate. Some time was usually required for the very scanty precipitate to assume an aggregation suitable for filtration.

The table given below records the time of boiling and the weight of argentic chloride found.

No. of experiment.	Time of boiling. Hours.	Weight AgCl found from residue. Gram.
1	2	0.0049
2	3	0.0047
3	3	0.0048
4	4	0.0054
5	7½	0.0050
6	8	0.0047
7	11½	0.0050
8	11½	0.0052
	Average,	0.0050

The constancy of figures in the last column is as great as could be expected ; it shows that all the acid which could be expelled was driven out at the end of two hours. Thus no essential amount of hydrochloric acid was lost after that time, and since the experiments with pure hydrocyanic acid showed that this acid could all be driven off, the precipitate must have consisted wholly of argentic chloride. Hence the average, 0.0050 gram, is a constant which may be used with future experiments involving the solution.

Two points remained to be proved. Could any of the hydrochloric acid have been carried off during the first two hours, and can the hydrocyanic acid be expelled as readily when much hydrochloric acid is present? Both of these questions may be easily answered by a series of experiments in which a known amount of potassic chloride is added to the standard solution of cyanide. In this series, recorded below, the method of experimentation was precisely similar to that employed in the earlier series. The mixed solution was diluted, treated with an excess of sulphuric acid, and boiled. From each weight of argentic chloride obtained from this solution was subtracted 0.0050 gram, the correction found above :

No. of experiment.	Weight KCl added. Gram.	Weight AgCl calculated. Gram.	Weight AgCl found (corr.). Gram.	Error. Milligrams.	Time of boiling. Hours.
9	0.0862	0.1657	0.1984	+32.7	2.0
10	0.2883	0.5541	0.5628	+ 8.7	4.0
11	0.0811	0.1558	0.1604	+ 4.6	4.0
12	0.0946	0.1819	0.1832	+ 1.3	6.0
13	0.0699	0.1343	0.1359	+ 1.6	8.0
14	0.0696	0.1338	0.1337	− 0.1	9.0
15	0.0653	0.1255	0.1262	+ 0.7	9.5
16	0.1738	0.3341	0.3342	+ 0.1	9.5
17	0.1282	0.2464	0.2472	+ 0.8	10.0

These results bring out several interesting points. In the first place, two hours' boiling, which amply sufficed when little or no potassic chloride was added, is now entirely inadequate to expel all the hydrocyanic acid. Thus, something in the solution must tend to hold back this acid. But the only important addition to the solution is the chlorine ion, hence the chlorine ion must tend to form a complex with hydrocyanic acid. The tendency of this ion to form complexes with various other undissociated groups has been noticed before, especially by Richards and Archibald,[1] so that this behavior is not startling, but it is nevertheless a matter of interest which will receive further attention in this laboratory.

Of more direct bearing upon the immediate object of the present research is the fact that after eight or nine hours' prolonged boiling this complex seems to be entirely broken up by progressive dissociation due to the steady volatilization of one of its components, and that this volatilization is effected without loss of hydrochloric acid. Thus it is shown that the method really affords a convenient and adequate means of separating quantitatively the two acids in question. Probably hydrobromic acid could be separated as easily as hydrochloric.

While the hydrocyanic acid might be collected and determined in the distillate, it would probably be easier to determine the amount by difference, precipitating both in one portion as argentic salts, and then precipitating argentic chloride alone in another portion, which had been evaporated in the manner described in this paper. The silver salts are so easily

[1] Proc. Am. Acad., **37**, 347 (1902).

weighed that this indirect method would not lead to serious error.

The outcome of this paper may be summed up as follows: A simple method is described for the quantitative analysis of mixtures of chlorides and cyanides, and evidence is given which indicates a tendency on the part of hydrocyanic acid to add to the chlorine ion.

CAMBRIDGE, MASS., Jan. 27, 1902.

ON THE NATURE OF MERCURIC IODIDE IN SOLUTION.

BY J. H. KASTLE AND JEWETT V. REED.

About two years ago it was shown by Kastle and Clark[1] that solutions of mercuric iodide in organic solvents have a yellow color and that from such solutions the yellow form of the iodide and not the red separates on crystallization. The effect of heating the red mercuric iodide with amyl alcohol, keeping the iodide in excess, was also tried. It was observed that a yellow solution of mercuric iodide was always obtained and that invariably a thin film of the yellow variety, or a little mass of yellow crystals, was found on top of the unchanged red iodide. The view was advanced, therefore, that when equilibrium is reached in such solutions there are as many molecules passing out of the solution as are passing in, and that both are molecules of the yellow variety of this compound. That the red iodide is not entirely changed to yellow by first passing into solution and then crystallizing out is probably due to the fact that by contact with a certain amount of the red variety remaining in the tube, the yellow is rapidly changed to red as it separates from the solution. We should, therefore, have the solvent constantly changing the red iodide to the yellow, then dissolving it and again precipitating it in the yellow form. This last, however, would tend to pass back to the red modification as soon as removed from solution. It will be observed, therefore, that the effect of solvents on the red iodide of mercury is essentially the same as that produced by heat; and that in the act of dissolving, the transition temperature of the iodide is greatly lowered.

[1] This JOURNAL, **22**, 473, 484.

In this connection it occurred to us to determine whether the yellow form of mercuric iodide could exist in equilibrium with its solution at temperatures below its transition-point, *viz.*, 128° C. With this in view, tubes were prepared containing amyl alcohol and red mercuric iodide, the latter in excess of that required to form a saturated solution at the given temperature. These tubes were then heated in the air-oven at 150° C. until a saturated solution of the iodide in amyl alcohol was obtained and until the excess of the iodide had been transformed to the yellow modification. The tubes were then placed in the vapor of boiling glacial acetic acid, 118° C. For some time after putting the tubes into the vapor of the acetic acid the yellow crystals of the iodide showed no alteration. In about ten minutes, however, red spots began to appear among the yellow crystals, indicating that no equilibrium was possible between the yellow variety of mercuric iodide and its saturated solution in amyl alcohol even at 10° below the transition temperature of the compound. These experiments were repeated several times with like result in every case.

Are Solutions of Mercuric Iodide Saturated with the Yellow or Red Modification of the Compound?

As was pointed out in our previous communication, the color of solutions of mercuric iodide is such as to indicate that they are saturated with respect to the yellow variety of this compound only. With the view of throwing still further light on this question, which, from a theoretical standpoint, is one of great importance, the attempt was made to prepare supersaturated solutions of the iodide in certain of these solvents, with the view of testing the conduct of such solutions towards crystals of the red and yellow variety of the compound. Considerable difficulty in the selection of a solvent was encountered at the outset in consequence of the great tendency on the part of the iodide to crystallize. Among the first solvents to be tried was amyl alcohol. It was found, however, that as soon as the supersaturated solutions of the iodide in this solvent were placed in tubes in order to make the necessary observations, a rim of yellow crystals separated on the top of the solution, thereby putting a stop to the experiment. It was found

that this difficulty could be overcome by employing naphthalene. After a number of preliminary observations, it was found that a supersaturated solution of mercuric iodide in naphthalene could be prepared by dissolving 1 part of the iodide in 20 parts of naphthalene. During the filtering of such solutions a small amount of naphthalene was unavoidably lost by evaporation. It was found that this could be compensated for by making the ratio of the mercuric iodide to naphthalene 1 : 20.1 or 1 : 20.25 instead of 1 : 20. As a general thing it was found expedient to make up a sufficient quantity of such a supersaturated solution for a whole series of experiments. This was done by melting 80 grams of naphthalene with the required amount of mercuric iodide in a tightly stoppered bottle. The solution thus obtained was usually slightly turbid and, hence, had to be filtered. This was done by filtering it through a folded filter-paper into another glass bottle, the filter-paper, funnel, and bottle having been previously heated in the air-oven to 140° C. In this manner a perfectly clear, yellow solution of mercuric iodide in naphthalene was obtained. With such solutions, experiments were conducted in the following manner :

A number of test-tubes, 6 x $\frac{3}{4}$ inches, were graduated in 10 cc. A pair of these tubes were then clamped together as close as possible by means of iron clamps which, in turn, were fastened securely to the wall of the laboratory. A glycerin-bath was then placed under the tubes, on the ring of an iron stand, and so arranged that it could be raised or lowered without disturbing the tubes. The bath, which consisted of a large beaker partly filled with glycerin, was then heated to 140° C., and the tubes so immersed therein as to have the 10 cc. mark on the tubes some little distance beneath the surface of the glycerin. By means of a long-necked funnel 10 cc. of the solution of mercuric iodide in naphthalene, which had been kept at 140° C. in the air oven, were poured into each of the tubes in the glycerin-bath. Thermometers, which had previously been heated to 140° C. in the air-oven, were then placed in the tubes and so arranged that their bulbs were entirely immersed in the solution without touching either the bottom or sides of the tubes. During this time the temperature of the

glycerin-bath was kept at 140° C. When everything had been thus arranged the glycerin-bath was quickly lowered and a bath of boiling water put in its place. This bath consisted of a large beaker about two-thirds full of boiling water and so arranged as to keep the level of the water always above that of the solution in the tubes. In about three minutes from the time the tubes were immersed in the boiling water they had reached a temperature of 100° C., and no mercuric iodide had as yet crystallized out of the solution. A few crystals of the red mercuric iodide, which had also been heated to 100° C., were now carefully dropped into the solution in one of the tubes, care being taken not to jar or shake the tube in any way. No crystals of either variety of the iodide separated on the addition of the red crystals. A few crystals of the yellow iodide, which had been heated to 100° C., were then dropped into the second tube, when a large crop of yellow crystals separated from the solution at once, whereas in the tube to which the red crystals were first added no crystals of any kind had separated up to this time. A few yellow crystals, warmed to 100° C., were then put into this tube, when a large crop of yellow crystals separated immediately. During all this time the tubes containing the solution of mercuric iodide were so immersed in the boiling water as to keep the level of the water always above that of the solution in the tubes. These experiments were repeated several times with exactly the same results in every case. Hence we must conclude that the solution of mercuric iodide in naphthalene is supersaturated with respect to the yellow iodide of mercury and not with respect to the red. That such is the case is borne out by the color of the solution. It was also observed that finely and coarsely powdered glass and powdered calc spar, heated to 100° C., caused the separation of yellow crystals from these supersaturated solutions of mercuric iodide in naphthalene, and a cold particle of almost any kind, or one heated below 100° C., was found to do the same. In view of the great tendency on the part of the mercuric iodide to crystallize, it occurred to us that the separation of crystals of this compound from its supersaturated solutions by the powdered glass and calc spar might in reality have been brought about by a low-

ering of the temperature of the solution by the solid particles rather than by the action of a truly isomorphous substance on the solution. Up to this time the substances to be added to the supersaturated solutions of the iodide had been heated in small test-tubes on the water-bath. In the last series of experiments on this phase of work the substances intended to be put into the supersaturated solutions of the iodide were heated in a small test-tube, surrounded by a steam jacket and so arranged as to bring the mouth of the small test-tube directly over the mouth of the larger tube containing the solution of mercuric iodide. In this way any cooling of the crystals was prevented. The following substances were tried under these improved conditions:

The yellow and red iodide of mercury, Iceland spar, sodium nitrate, hematite, siderite, celestite, fluor-spar, carborundum, and finely powdered glass, coarsely powdered glass, gypsum, and dolomite. The red and yellow iodide of mercury were added in the form of small crystals, the other substances in the form of coarse powder. Of these substances the following were found to throw out crystals of the yellow iodide of mercury from the supersaturated solutions of mercuric iodide in naphthalene: The yellow iodide of mercury, finely powdered glass, Iceland spar, sodium nitrate, siderite, hematite, celestite, fluorspar, and carborundum. On the other hand, the red iodide of mercury, coarsely powdered glass, gypsum, and dolomite caused no separation of crystals of any kind from the supersaturated solutions of the iodide. It is interesting to note in passing that of those substances that precipitate yellow mercuric iodide from its supersaturated solution a number of them are rhombic in crystal form like the yellow iodide of mercury itself. The fact, however, that the yellow iodide is also thrown out of its solutions by substances of different crystal habit and even by sharp-pointed fragments, such as glass, would seem to indicate that the precipitation of the yellow iodide from its supersaturated solutions is not necessarily brought about by the action of isomorphous crystals but also by the disturbance of an unstable condition of equilibrium in the supersaturated solutions of the iodide. That such is the case would also seem to be indicated by the fact that even

those substances of the same crystal form as the yellow iodide of mercury, such as calc-spar, siderite, and hematite, are insoluble in naphthalene, and therefore probably incapable of acting as true isomorphous substances on the solution of the yellow iodide of mercury. However this may be, the fact remains that the yellow iodide of mercury and not the red variety of this compound precipitates the yellow iodide from supersaturated solutions of mercuric iodide in naphthalene, and it is further interesting to note that the yellow iodide is the only form of the compound ever precipitated from its supersaturated solutions by any substance. Either the yellow iodide is thrown out of these supersaturated solutions or nothing at all. These facts, therefore, strongly support the conclusion already advanced in the former communication on this subject, *viz.*, that solutions of mercuric iodide really contain the yellow modification of this compound and not simply molecules of the iodide, HgI_2, which may arrange themselves in the yellow or red form of the compound according to the nature of the crystal which is first presented to them.[1] It would seem, therefore, that red mercuric iodide changes to yellow in the act of passing into solution. In this connection it has been observed repeatedly that the yellow iodide seems to dissolve more readily and rapidly in organic solvents than the red. In order to determine whether such was really the case the rate of solution of the yellow and red iodide was tried in naphthalene, in the following manner:

Two portions of naphthalene, of 15 grams each, were weighed out and put into two glass-stoppered bottles of the same size and shape. These two bottles were clamped firmly together and placed in a bath of boiling water. Two equal portions of mercuric iodide were then weighed out, the quantity taken being in excess of that which 15 grams of naphthalene would dissolve at 100° C. One of these portions was then gently heated so as to convert it into the yellow modification

[1] In this connection certain recent observations of Wegscheider and Kaufler on the allotropy of phosphorus are worthy of note. According to these observers a saturated solution of yellow phosphorus in carbon disulphide sown with red phosphorus shows no perceptible change, and, on lowering the temperature, yellow phosphorus separates. They have reached the conclusion, therefore, that these two forms of phosphorus are not polymorphous, but chemically different (Monatsh. Chem., **22**, 700–706 (1901)).

and then quickly cooled to the ordinary temperature again. The red portion of the iodide was then put into one of the bottles of naphthalene and the yellow portion into the other. Both bottles were then tightly stoppered and vigorously shaken for a short time, after which they were put back in the water-bath. After a few minutes the bottles were removed from the bath and 5 cc. of each of the solutions drawn out by means of a pipette, which had been heated to 100° C. These two portions of the solutions were then boiled with water and zinc dust and filtered and the amount of iodide in each determined volumetrically with N/10 silver nitrate. In this way 5 cc. of the solution that had been prepared from the red mercuric iodide was found to contain 0.124 gram of mercuric iodide, whereas 5 cc. of the solution that had been prepared from the yellow iodide was found to contain 0.158 gram of mercuric iodide. A second experiment, carried out exactly like the first, gave for the same amounts of solution the following numbers respectively; *viz.*, 0.122 gram and 0.144 gram of mercuric iodide. It would seem, therefore, that the yellow mercuric iodide dissolves more rapidly in naphthalene than the red. The results are in harmony with the view already advanced in our former communication, *viz.*, that the red iodide is insoluble in these solvents and that in the act of solution it is changed to the yellow form of the compound, which then dissolves at once. The fact that the red iodide dissolves more slowly than the yellow is in support of this conclusion.

The Stability of the Yellow Mercuric Iodide under Different Solvents.

The stability of the yellow mercuric iodide varies greatly under different solvents. When crystallized from ethyl alcohol, acetone, benzene, toluene, ethyl iodide, ethylidene chloride, ethyl cyanide, and phenyl cyanide the yellow iodide thus obtained changes to red very rapidly under the solvent, whereas, when crystallized from amyl alcohol, allyl alcohol, naphthalene, isobutyl bromide, ethyl butyrate, methyl salicylate, and phenyl salicylate it changes to red very slowly under the solvent. That the solvent actually exerts some influence on the stability of the yellow iodide is seen from the fact that

the yellow iodide obtained by crystallization from ethyl iodide changes rapidly to red if allowed to remain under the solvent, whereas if removed from the solvent and dried in the air it is only slowly changed to red. In one batch of crystals thus prepared and allowed to stand in the air a number of yellow ones were found after two and a half days. On the other hand, under ethyl butyrate the yellow iodide is very stable, whereas the same crystals, when exposed to air and not in contact with the solvent, were found to alter very rapidly. There are doubtless many peculiarities connected with the action of various solvents on the labile form of this compound which as yet cannot be satisfactorily explained. On the other hand, in studying the stability of the yellow iodide under different solvents, it soon occurred to us that its stability under the solvent increases with the viscosity of the latter. That such is the case is rendered evident by a comparison of its stability under ethyl and amyl alcohol, benzene, and naphthalene, respectively. It was also observed that light accelerates the change of the yellow iodide into the red, under all solvents. It therefore occurred to us that the yellow iodide could be preserved unchanged for a considerable time provided it were crystallized from a very viscous solvent and kept in the dark. The following experiments were therefore tried in order to determine whether such was really the case: Very concentrated solutions of mercuric iodide in glycerin were prepared by heating the iodide in glycerin to 200° C. in perfectly clean test-tubes. On cooling, these solutions deposited very minute crystals of the yellow iodide. The tubes were then placed in the dark room. The first tube thus prepared showed no trace of the red compound until one week after it had been made. At the end of two weeks the red iodide was pretty well diffused throughout the tube. Another tube prepared in exactly the same way showed no trace of the red compound for two weeks, and at the end of five weeks there was only a thin layer of red crystals on the surface of the yellow ones. Two tubes of the yellow iodide in glycerin were then prepared by pouring a hot solution of the iodide in glycerin into cold glycerin. In this way the yellow iodide was precipitated in even smaller crystals than by crystallizing

from the hot solution. These tubes remained unchanged for two weeks, at the end of which time crystals of the red iodide were seen diffused throughout the mass of the yellow compound. It was thought that possibly the friction of the yellow crystals against the walls of the test-tube might have caused the change of the yellow to red. In order to do away with this, if possible, a solution of the iodide in glycerin, containing the fine yellow crystals in suspension, was poured into small cups made of paraffin. Under these conditions the yellow iodide remained unchanged for two weeks, at the end of which time red crystals began to make their appearance. It will be observed, therefore, that the paraffin vessels offered no particular advantage over the test-tubes.

The next solvent tried was a very thick, concentrated solution of cane-sugar. Under this solvent the yellow iodide remained unchanged for several days, after which the mass of yellow crystals gradually became red. In this connection it should be observed that under water the yellow iodide of mercury is very unstable, so that the cane-sugar, by increasing the viscosity of the solution, greatly increases the stability of the yellow iodide.

The conduct of the yellow iodide under vaseline was next studied. Mercuric iodide was dissolved in boiling vaseline and the solution allowed to cool. The yellow iodide separated on cooling and the vaseline became gelatinous. One tube prepared in this manner and placed in the dark room showed absolutely no trace of red at the end of nine weeks. At the end of this time a few of the yellow crystals turned red, but even now, one year and seven months since this tube was prepared, probably not more than 25 per cent of the yellow crystals have changed to red. Another tube containing the yellow iodide and vaseline was prepared on the 14th of April, 1900. To-day, Nov. 12, 1901, this tube shows no red crystals except in the upper part of it, where a little of the solution stuck to the walls of the tube when it was poured in. Otherwise the yellow iodide under the vaseline remains unchanged and is as pure yellow now as it was the day that it was put in the tube. Yellow mercuric iodide is more stable in contact with vaseline than any solvent thus far studied.

The fact that the yellow iodide is more stable in contact with viscous solvents than with those that are very mobile is in harmony with the general conduct of these two classes of solvents and can, therefore, be readily explained. In viscous solvents all chemical and physical changes are slow, sudden changes of temperature are practically impossible, and the motion and rubbing of suspended particles but slight. When these facts are kept in mind and we consider also the general reluctance on the part of all substances to form new phases, we can readily understand why the yellow mercuric iodide resists alteration in viscous solvents.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Nov., 1901.

Contributions from the Sheffield Laboratory of Yale University.

XCI.—ON BENZOYLBENZYLUREA, BENZOYLPARATOLYLUREA AND THE CORRESPONDING PSEUDOETHYLUREAS: A CORRECTION.

BY HENRY L. WHEELER AND TREAT B. JOHNSON.

In our article on the behavior of acylthioncarbamic esters with alkyl iodides and amines[1] we described products obtained by the action of benzylamine and paratoluidine on ethyl benzoylthioncarbamate, which, from our analytical data, were concluded to be benzoylbenzyl and benzoylparatolylurea.

The compounds melted at 89° and 80°, respectively. The fact that these are abnormally low melting-points for benzoylureas escaped our notice until recently, whereupon, on making a reexamination of the products, it was found that they are not normal but pseudoureas.

Pure benzoylpseudoethylparatolylurea,

$$C_6H_5CON = C(OC_2H_5)NHC_6H_4CH_3,$$

prepared from ethyl benzoylimidothiocarbonate boiling at 104° at 16 mm. pressure, is a solid that can be repeatedly recrystallized from strong alcohol, and it melts sharply at 75°. When this is treated with dilute hydrochloric acid, ethyl chloride is evolved and the material is smoothly transformed into

[1] This JOURNAL, 24, 208, 209 (1900).

benzoylparatolylurea, melting at 222° to 223° and not at 80°.

Some of the original material melting at 89° which was described as benzoylbenzylurea, when treated with hydrochloric acid, also evolved ethyl chloride and passed smoothly into the true benzoylbenzylurea, melting at 165° to 166°.

These amines, like ammonia, therefore react on ethyl benzoylthioncarbamate with evolution of hydrogen sulphide and formation of pseudoureas as follows:

$$C_6H_5CONHCSOC_2H_5 \rightarrow C_6H_5CONH(HS)C(NHR)OC_2H_5 \rightarrow C_6H_5CON{=}C(NHR)OC_2H_5.$$

Benzoylpseudoethylparatolylurea crystallizes from alcohol in colorless, small, flattened prisms melting at 75°.

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.92	10.1

Benzoylparatolylurea, from the above and hydrochloric acid, crystallizes from alcohol, in which it is difficultly soluble, in the form of needles, melting at 222° to 223°.

	Calculated for $C_{15}H_{14}O_2N_2$.	Found.
N	11.02	10.87

Benzoylpseudoethylbenzylurea forms colorless, flattened prisms or plates from alcohol, melting at 89° to 90°.

	Calculated for $C_{17}H_{18}O_2N_2$.	Found.
N	9.92	10.03

Benzoylbenzylurea forms colorless prisms from alcohol, melting at 165° to 166°.

	Calculated for $C_{15}H_{14}O_2N_2$.	Found.
N	11.02	11.28

NEW HAVEN, CONN.,
Feb. 4, 1902.

REPORTS.

The Molecular Weight of Sulphur.

That at high temperatures sulphur vapor exists as the molecule S_2 has never been doubted since the work of Troost,[1] Bineau,[2] and of V. and C. Meyer.[3] Especially has the work of Victor Meyer alone and in company with Biltz[4] established the existence and constancy of this molecule, S_2, between the temperatures 900° and 1700° C.

For a long time also, based upon the measurements made by Dumas,[5] Mitscherlich,[6] and V. and C. Meyer,[7] the density of sulphur vapor at temperatures between 490° and 530° was placed at about 6.6. The mean of the various determinations are:

Dumas	6.64
Mitscherlich	6.57
V. and C. Meyer	6.63

These lead to a molecular weight of 192. That is the sulphur molecule exists as S_6.

The first to cast doubt on the existence of the six-atom molecule was Biltz,[8] in 1888, although Liebig, previous to 1840, had determined the molecular weight of sulphur by Dumas' method but had found such large differences in his values that he had never published them. This fact remained unknown until after the publication of the correspondence of Liebig and Berzelius.

Biltz determined the density of sulphur vapor at various temperatures between 468° and 606° by both the Dumas and the Victor Meyer method. Most of his determinations were made at 518° and 606°, using the vapor of phosphorus pentasulphide, and zinc chloride as the heating agents. Between 468° and 606° the vapor was found to vary in density from 7.3 to 3.5 by the Victor Meyer method, and between 7.8 and 4.7 by the Dumas method.

The values obtained by the method of V. Meyer were always lower than those obtained by the Dumas method at the same temperature. These discrepancies Biltz explains as due to the nitrogen used as the gas to be displaced in the Victor

[1] Ann. chim. phys., [3], **58**, 257.
[2] *Ibid.*, [3], **59**, 456.
[3] Ber. d. chem. Ges., **12**, 1115.
[4] Ztschr. phys. Chem., **4**, 266.
[5] Ann. chim. phys., **50**, 178; Pogg. Ann., **21**, 559.
[6] Pogg. Ann., **29**, 217.
[7] Ber. d. chem. Ges., **11**, 2259.
[8] *Ibid.*, **21**, 2013; Ztschr. phys. Chem., **3**, 920.

Meyer method. He found that when the quantity of sulphur used in his experiments was increased, and when precautions were taken to prevent the rapid diffusion of the sulphur vapor into the nitrogen, the density approached more nearly to that obtained by the Dumas method.

As the result of his work, Biltz concluded that there was no ground for the assumption of the existence of the molecules S_8, S_8, or S_{10}, and that the increase in density observed as the temperature of the experiment was lowered was not due to an association of the simpler molecules, but that at the lower temperatures the deviations from the gas laws shown by the vapor were very much greater than at higher temperatures. He also concluded that the density corresponding to the molecule S_2 was the only one which remained constant over any considerable range of temperature.

Biltz's conclusion that he had proved the non-existence of the molecule S_6 was soon challenged. Ramsay[1] pointed out that Biltz's results had not proved, to him at least, the non-existence of a sulphur molecule containing 6 atoms.

Biltz,[2] in reply, admitted the possibility of the molecule S_8, but stated that he had not worked over a sufficiently large range of temperature to prove its existence. The existence of the molecule S_6 he would not admit.

Riecke[3] used Biltz's results as a groundwork to deduce a law governing dissociation by steps, as well as to show mathematically that the sulphur molecule passes from S_8 to S_2 with the intermediate formation of the molecule S_6 according to the equation

$$S_8 = S_6 + S_2;$$
$$S_6 = 3S_2.$$

Nernst[4] and Ostwald,[5] in their text-books, have also emphasized the fact that the non-existence of the molecule S_6 had not been proved.

C. Schall,[6] using a method devised by himself for measuring densities under diminished pressure, and hence, at lower temperatures, gives the value S_8, and concludes with Biltz that the molecule S_6 is non-existent.

Krause and V. Meyer[7] have also given the value S_8 at temperatures below the boiling-point of sulphur under atmospheric pressure. Neuberg[8] has also arrived at the same conclusion.

[1] Ztschr. phys. Chem., **3**, 67.
[2] *Ibid.*, **3**, 228.
[3] *Ibid.*, **6**, 430.
[4] "Lehrbuch der allgemeinen Chemie," 2nd Ed., Vol. I., p. 2188.
[5] "Theoretische Chemie," 2nd Ed., p. 415.
[6] Ber. d. chem. Ges., **23**, 919, 1701 (1890).
[7] Ztschr. phys. Chem., **6**, 5 (1890).
[8] Ber. d. chem. Ges., **24**, 2544 (1890).

Paterno and Nasini[1] were the first to determine the molecular weight of sulphur in solution by the cryoscopic method. They thought that they had established the existence of the molecule S_8 in benzene as a solvent.

Beckmann,[2] using carbon bisulphide as a solvent, made it very probable that the molecule S_8 does exist, although he could not with certainty exclude the existence of S_9.

Hertz,[3] using naphthalene, obtained a value S_8 for the molecule. By the boiling-point method, Helff,[4] with carbon bisulphide as a solvent, reached the same conclusion as Beckmann.

Sakurai[5] and Biltz,[6] using nitrobenzene, obtained a molecular weight between S_7 and S_8. Later Orndorff and Terasse,[7] in boiling naphthalene, xylene, and phenetol, and in freezing diphenyl, found the value S_8, but in freezing naphthalene the value S_7, while in sulphur monochloride they obtained S_2, and in boiling toluene and carbon bisulphide found the molecule S_8.

Gloss[8] has given for the different modifications of sulphur values between S_8 and S_9, working with naphthalene by the freezing-point method.

Barnes,[9] working in carbon bisulphide, has obtained the value S_8.

The work of Orndorff and Terasse has been completely contradicted by Aronstein and Meihuizen,[10] who worked with solutions in toluene, xylene, naphthalene, and carbon bisulphide, both above and below the transition-point of rhombic to monoclinic sulphur, and above and below its melting-point. They obtained a constant value S_8.

It seems, then, to be settled that at high temperatures sulphur exists as S_2, while at low temperatures and in solution it exists as the molecule S_8. But this question still remains to be settled: How does the molecule S_8 break down? Does it pass at once to the molecule S_2 or do we have an intermediate formation of S_6, as has been generally accepted?

In the last year or two, two important papers bearing on this point have appeared.

Bleier and Kohn[11] have used in their experiments a modification of the method of Victor Meyer, in which, instead of measuring the volume of gas displaced by the substance whose

[1] Ber. d. chem. Ges., **21**, 2153 (1888).
[2] Ztschr. phys. Chem., **5**, 76 (1890).
[3] *Ibid.*, **6**, 358.
[4] *Ibid.*, **12**, 200.
[5] J. Chem. Soc., 1892, 989–1002.
[6] Ztschr. phys. Chem., **19**, 425.
[7] This JOURNAL, **18**, 173.
[8] J. Phys. Chem., **2**, 451.
[9] *Ibid.*, **3**, 151.
[10] Verh. der Königl. Akad. Wiss., Amsterdam, July, 1898; Centrbl., (1898), II., 1194; (1900), I., 392.
[11] Monatsh. Chem., **20**, 505, 909; **21**, 575.

vapor-density is to be measured, they have measured the change in pressure produced when the apparatus is connected with a manometer.

Their calculations are based on the gas law that equal numbers of gram-molecular weights of various substances, when in the gaseous state, produce equal changes in pressure under similar conditions of temperature and volume.

The above manner of stating the underlying gas laws is similar to the Van 't Hoff law of osmotic pressure, which forms the foundation of the Raoult-Beckmann method of determining molecular weights.

They use this gas law to determine the molecular weights of substances when vaporized, as the Van 't Hoff law is applied to solutions for determining the molecular weight of substances in solution. The pressure change produced by the milligram-molecular weight of any substance when vaporized in the apparatus at a known temperature is called the constant of the apparatus for this temperature. Hence:

$$q : p = m : c;$$

or

$$m = \frac{qc}{p},$$

where m is the molecular weight of the substance to be determined.

q is the weight of the substance vaporized in the apparatus.

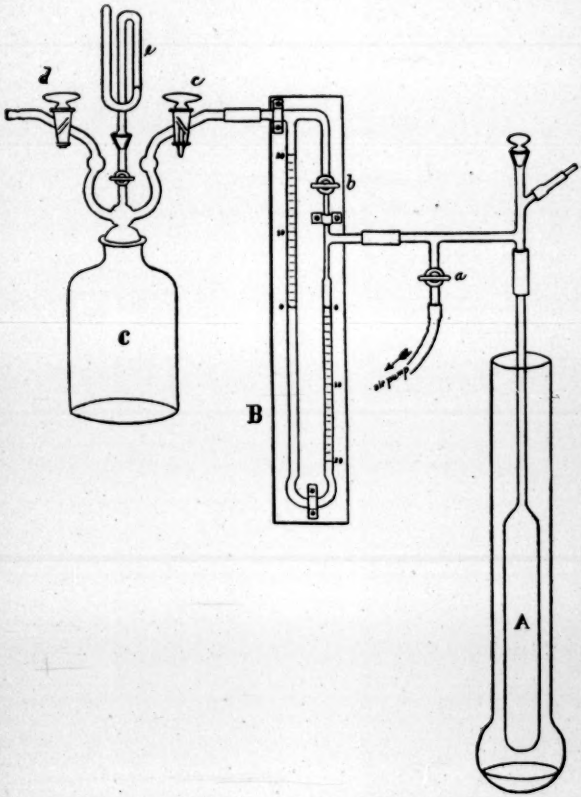
c is the constant as explained above.

p is the change in pressure observed when q is vaporized.

The following cut shows their apparatus as used in the determination of the molecular weight of sulphur.

A is the vessel in which the substance is vaporized. B is the manometer. The arms communicate with one another both below and above as long as this last communication is not broken by the closing of *b*. The manometer is filled with a paraffin oil of high boiling-point (400° to 500°), whose specific gravity is between 0.7 and 0.8. Hence a difference of pressure equivalent to 2 mm. of mercury would show on this manometer a difference in level of 35 mm. The length of the manometer arms is sufficient to show a change in pressure of 400 mm., which is equivalent to 24 mm. of mercury. C is a vacuum reservoir closed by a ground-glass stopper with three openings. *c* and *d* are stop-cocks, *c* being a three-way cock containing a very fine hole for the admission of air to the apparatus. *e* is a small mercury manometer. *a* connects with an air-pump.

In carrying out a determination, the substance is suspended


d
e
f
C
B
b
a
A

in a small tube at *f*. The stop-cock *b* being open, the whole apparatus is pumped out to the desired pressure, while the liquid in the jacket surrounding A is boiled. The stop-cock *b* is then closed. The substance is allowed to drop to the bottom of A, when it is vaporized. As soon as the manometer becomes constant the difference in the level in the two arms is read. This gives the necessary data for the calculation of *p*, and, hence, of *m*, the molecular weight.

Using this method, Bleier and Kohn have established the dissociation isothermals of sulphur vapor over considerable ranges of pressure, at the temperature of boiling diphenylamine (310°), amyl benzoate (262°), quinoline (236°), ethyl benzoate (214°), and dimethylaniline (192°).

The density of the sulphur-vapor increases regularly with increase in pressure. The following table shows the least and greatest densities obtained at the various temperatures:

Temperature.	Pressure in mm. of mercury.	Density. $O_2 = 1$.
310°	42.5	7.43
310°	1.6	5.80
262°	18.4	7.49
262°	1.5	6.66
236°	9.4	7.66
236°	1.4	6.92
214°	4.2	7.80
214°	1.2	7.20
192°	2.1	7.85
192°	0.9	7.48

From their results, and from the curves which they have plotted from these results, it is seen that the values for the densities gradually approach the value 8, and in the pressure-density curve become asymptotic to this value. From this they conclude that the undissociated sulphur molecule is S_8.

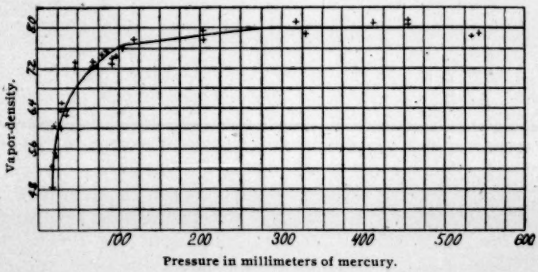
If the molecule S_8 exists, as Riecke had concluded from a theoretical consideration of Biltz's results, as has already been mentioned, it would be expected that the density 6 would be found to remain constant over a considerable range of pressure. In the results obtained at 310°, the only temperature at which densities were found lower than 6, no trace of any such constant value was observed and the curves show no tendency to depart from their regular form. These results would point to the non-existence of the molecule S_8, but Bleier and Kohn conclude that, to settle this point definitely, dissociation isothermals at higher temperatures are necessary as well as to

obtain densities lower than 5.80, the lowest obtainable at the highest temperature at which they worked.

Biltz and Preuner[1] have completed the proof necessary to completely exclude the molecule S_8 by a series of experiments, using the Dumas method under diminished pressure.

The principle of their apparatus is in general that of Habermann,[2] but special modifications have been introduced to meet the difficulties of their experiments. Their determinations were made at the temperature of sulphur boiling under atmospheric pressure, and at pressures varying between 14.0 and 539.2 mm. of mercury.

The greatest care and a high degree of accuracy are shown in the work. The sulphur used was subjected to five distillations before use. As the quantity used in an experiment was very small, especially under the lower pressures, analytical methods for determining the amount of sulphur in the Dumas bulb were employed in order to avoid the errors due to weighing very small amounts. In all, thirty-two determinations were made which show a gradual rise in density with increase in pressure. No evidence of the existence of the six-atom molecule was found, as is seen by a study of the following curve. Not the slightest tendency for the curve to straighten out or show irregularities is noticed in the neighborhood of density 6.



In conclusion, it has been shown that at the lowest temperatures at which sulphur can be vaporized it exists as S_8. As the temperature rises, this commences to break down into the molecules of S_3, while at temperatures above 900° sulphur exists solely as S_2. In solutions it exists as S_8.

CHARLES F. LINDSAY.

[1] Monatsh. Chem., **22**, 627; Ber. d. chem. Ges., **43**, 2490; Ztschr. phys. Chem., **34**, 323.

[2] Ann. Chem. (Liebig), **187**, 341 (1877).

Sulphuric Acid and Its Preparation by the Contact Method.

Since the announcement made several years ago that a successful catalytic method for the preparation of sulphuric acid in large quantities was in use at the Badische Anilin- und Soda-Fabrik, chemists have been anxious to obtain all the information possible regarding the process. The German Chemical Society could not have selected a better person to speak on this subject than R. Knietsch, who is connected with the Badische Anilin- und Soda-Fabrik, and who has taken an active part in the successful application of the method. In a very interesting lecture[1] delivered at the Hofmann-House, Oct. 19, 1901, he sketched the story of the solution of the problem and furnished valuable additions to our knowledge of sulphuric acid.

After referring to the important rôle that the acid has always played in inorganic chemistry and its growing importance in the domain of organic chemistry, owing to its extensive use in the manufacture of alizarin and synthetical indigo, he pointed out the extreme theoretical simplicity of the reaction when oxygen and sulphur dioxide combine, a reaction which, however, is very slow and requires the assistance of a catalytic agent. In the old method a gaseous agent was used and a dilute acid was obtained, but in the improved method a solid, practically permanent, agent is used and solid sulphur trioxide is obtained. In studying the historical development of the subject four periods can be recognized.

The first period began with the discovery, made by Peregrine Phillips, Jr., of Bristol, who took out an English patent in 1831, of the catalytic action of platinum in the formation of sulphuric acid. Humphry Davy had discovered the catalytic action of platinum as early as 1817, and had studied its action on a mixture of oxygen or air with hydrogen, carbon monoxide, ethylene, and other gases; but neither he nor Döbereiner applied it in the preparation of sulphuric acid.

Seventeen years after Phillips' discovery Schneider, a Belgian chemist, supposed that in the discovery of the catalytic action of pumice stone the problem had been solved; but his great expectations were not realized. In 1846 a patent was issued to Jullion for the use of platinum asbestos as a catalytic agent, but it was not until later, and by others than the discoverer, that it was used in the preparation of sulphuric acid.

The second period was marked by the discovery made by Wöhler and Mahla that the oxides of copper, iron, and chromium also act as catalytic agents. They found that the oxides

[1] Ber. d. chem. Ges., 34, 4069.

of copper and iron, in the absence of oxygen, were reduced by the sulphurous acid with the formation of sulphuric acid, the latter being formed as long as there was any oxide to oxidize the sulphurous acid, while with the oxide of chromium, which was not reduced, no sulphuric acid was formed unless oxygen was present. These and similar experiments enabled them to explain the phenomena and formed the basis of the later work of Lunge and that described in this paper. A number of patents were granted during this period for the use of a variety of substances as catalytic agents, but fuming sulphuric acid could not be made, by any of these methods, at a price which would enable it to compete with that made by the distillation of iron sulphate.

We come now to the turning-point, to the work of Clemens Winkler. As a result of experiments, Winkler concluded that only a stoichiometrical mixture of two volumes of sulphurous acid and one volume of oxygen would form sulphuric acid, and that the presence of any other gas, even an excess of oxygen, would retard and decrease the action. He obtained the necessary mixture by heating sulphuric acid, forming water, oxygen, and sulphur dioxide, and condensing the water. The oxygen and sulphur dioxide, in the presence of the contact mass, unite to form sulphur trioxide. This work was of great importance and led to the manufacture of the fuming acid by a method which could compete with the ferrous sulphate method, which had had a monopoly of the field. Ten years later a process was devised for the use of air instead of pure oxygen, the retarding influence of the nitrogen being overcome by carrying on the action under pressure. None of these methods, however, enabled them to use the furnace gases or to compete with the chamber process for making dilute acid. Although it was considered impossible to use the furnace gases, the great importance of a cheap method for the manufacture of the pure acid led the Badische Anilin- und Soda-Fabrik to undertake a thorough investigation of the subject. As the residual gases in the chamber process contain 6 per cent of oxygen by volume, and as the furnace gases, after being in contact with the contact mass, also contain an excess of oxygen, it was difficult to understand why there was an incomplete formation of acid. Experiments made on the small scale with pure gases showed that with even strongly diluted gases the yield was almost quantitative and the dilution, if anything, increased the yield.

This observation disproved the results of Winkler regarding the retarding action of diluting gases and led to an exhaustive study of the conditions influencing the reaction.

The same experiments were carried out with the natural furnace gases, which were conducted into the laboratory through long lead pipes. These pipes served the purpose of collecting the solid particles. After the gases had passed through several vessels of sulphuric acid, they were brought in contact with the catalytic agent, and an excellent yield of acid was obtained, the mass seeming to retain its full power even after several days. When similar experiments were made on the large scale, however, the contact mass rapidly became inactive, even though the gases, in addition to being subjected to other methods of purification, were filtered through coke and asbestos filters, and were as pure as is possible on the large scale. An examination of the furnace gases showed that, while the action on the contact mass was due partly to the presence of antimony, bismuth, lead, zinc, and other substances in small quantities, the most injurious substance was arsenic, which was able, when present only to the extent of 1 to 2 per cent, to poison the mass and render it entirely inactive. The removal of the small amount of arsenic trioxide present in the gases as a mist was a problem which had been studied by many chemists, but had never been successfully solved.

After the expenditure of an immense amount of time, patience, and money a method was devised by which, through cooling and washing and other processes, the exact details of which are not given, the gases were *absolutely* freed of all impurities, especially those in the solid condition. It was found that the ease with which the solid particles could be precipitated depended largely upon the rate of cooling, slow cooling greatly facilitating it. Although it was supposed that acid of a concentration of 90 per cent would not act on iron, or, if so, would form sulphur dioxide, the decrease in power of the contact mass, which only began to appear after weeks or months, was shown to be due to the formation of hydrogen from the iron and sulphuric acid and the action of this on an arsenic compound to form arsine. Even the trace of arsenic contained in the small amount of sulphur, which passed through unprecipitated, was sufficient to injure the contact mass. But this was easily removed, as was also the sulphuric acid which was formed in the furnace and which before had acted on the iron and the arsenic compounds, by spraying the gases after they issued from the furnace where the pyrite was burned.

In the technical preparation of the fuming acid very little attention had been paid to the heat evolved when sulphur dioxide and oxygen combine, although it amounted to 22,600 cal. It was shown that the commonly accepted idea of the

necessity of heating the contact mass very high, in order to produce the combination when the diluted furnace gases were used, was incorrect, and that both the yield and the life of the mass could be increased if the tubes containing it were cooled in order to carry off some of the heat generated in the chemical combination of the two gases. A form of furnace was devised, something like a tubular boiler placed on end, and the contact mass arranged in the upright tubes of the furnace in such a way that the pressure and amount of surface of the mass exposed in each tube was the same. Under these conditions the process is a continuous one and the mass retains its full power for a year or more.

The ordinary method of absorbing gases by passing through a series of vessels containing water or dilute acid, would not entirely remove the sulphur trioxide even when a number of the absorbing flasks were used; but one vessel containing acid of 97 to 98 per cent sulphuric acid absorbs it instantly and entirely.

In order to keep the concentration at this point the excess of sulphur trioxide is removed from time to time or water is added. By the method just described the experimenters were able to obtain acid of any concentration and mixtures of the acid and sulphur trioxide in all proportions. A careful study of the properties of acids of different concentration showed not only interesting facts regarding the variations of the same property with acid of different strength, but also that the dif-

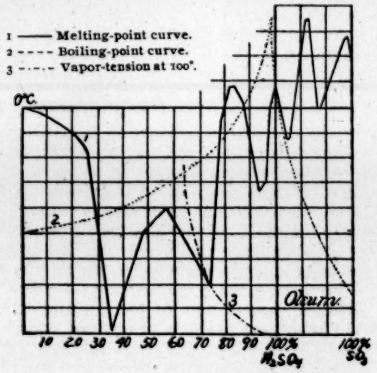


Fig. I.

ferent properties of the acid of the same concentration varied in the same way. In order to show the results in a clear manner they have been plotted in curves.

An examination of the curve representing the boiling-point (Fig. I., 2) will show that it increases from both sides until a

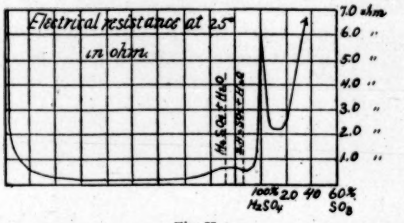


Fig. II.

maximum is reached in an acid of 98⅓ per cent. Starting with a more dilute acid and heating the solution, there is a loss of water until the concentration reaches that of the acid just referred to, after which the rest of the acid distils over at a constant pressure and as a definite substance, while, starting with a more concentrated acid, there is a loss of sulphur trioxide until the same concentration is reached as before, when the same results are obtained.

The curve representing the vapor-pressure (Fig. I., 3) diminishes gradually and reaches a value of zero at a point corresponding to the 98⅓ per cent acid. The electrical resistance (Fig. II.) begins to increase very rapidly when the 98⅓ per cent acid is reached, after having reached a maximum at a point corresponding to a compound of the formula $H_2SO_4 + H_2O$. It then decreases and finally ascends rapidly. Although cast-iron is not readily attacked by concentrated sulphuric acid, the oleums (the term used for the mixtures of the acid and sulphur trioxide) sink into the pores of the iron and generate there sulphur dioxide, hydrogen sulphide, and carbon dioxide from the carbon in the iron. The critical temperatures of these gases are low, and under these conditions the pressure sometimes becomes sufficient to cause explosions. Wrought iron (Fig. III.), on the other hand, which is attacked by concentrated sulphuric acid and even by the oleums of 10 to 15 per cent is not acted on at all by oleum containing more than 27 per cent sulphur trioxide. Weber has shown that pure sulphur trioxide melts at 17°.7. If now water is slowly added, the melting-point will rise until with an acid

containing 85 per cent sulphur trioxide a maximum is reached at 27° (Fig. I., 1). This applies, however, only to freshly prepared specimens as, after standing, they polymerize and no longer melt, but sublime at a higher temperature. With further dilution it reaches, with an acid containing 60 to 65 per cent of the trioxide, a melting-point of 0° to 2°, and, rising again, reaches a maximum at 36°, the acid corresponding to the formula $H_2SO_4 + SO_3$. This point is of special interest, as it coincides with the point of greatest pressure, the greatest

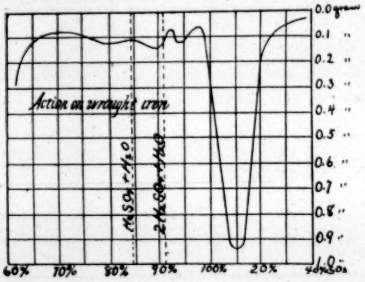


Fig. III.

viscosity, and a break in the curve of capillarity. With further dilution we find at −12° an acid which will attack the iron, at +10° one represented corresponding to the monohydrate, at −35° the acid $2H_2SO_4 + H_2O$, and at +8° the acid $H_2SO_4 + H_2O$.

The author also showed the results obtained from a study of the specific heat, heat of solution, capillary rise, and viscosity of acids of all concentrations. In the case of the viscosity, which increases as the concentration of the acid increases, until an acid containing 50 per cent oleum is reached, when it begins to decrease again; the values for water and pure sulphur trioxide were found to be identical.

Furnace gases which contained, besides nitrogen, a stoichiometrical mixture of oxygen and sulphur trioxide, when brought in contact with the catalytic mass at different temperatures and at different rates of flow, never gave more than 77 to 91 per cent of the theoretical yield; but, if one of the gases was present in excess, the other was completely removed. The curves S and S' in Fig. IV. represent the results with the stoichiometrical mixture.

The technical furnace gases formed by the roasting of pyrites contain about 7 volumes of sulphur dioxide, 10 volumes of oxygen, and 83 volumes of nitrogen. If this mixture is passed through an empty porcelain tube there is a small

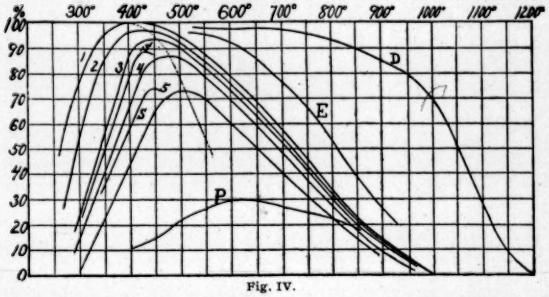
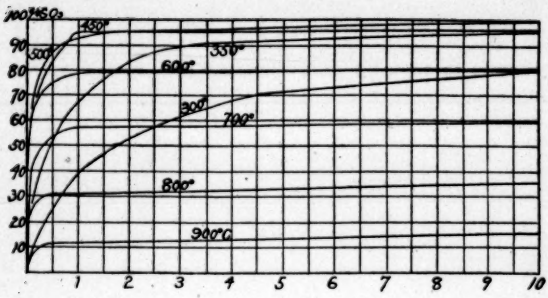


Fig. IV.

yield of acid (Fig. IV., *P*), but if a contact mass, as platinum asbestos, is placed in the tube, even at 200° the gases begin to combine, the yield increasing up to 400°–430°, where 98 to 99 per cent of the theoretical yield is obtained. As the temperature rises higher the acid is decomposed, the yield at 700° to 750° being only 60 per cent and at 900° to 1000° becoming practically zero.

If the amount of contact mass is diminished or, what is the same thing, the rate of flow increased the results represented in curves 1, 2, 3, 4, and 5 were obtained. While these are in general parallel they still show a tendency to diverge as they approach the point of maximum yield and then approach one another, reaching the zero point at about 900° to 1000°. As the rate of flow increases not only does the yield decrease, but the temperature at which the maximum yield is obtained becomes greater, as is indicated by the dotted line. Experiments with empty tubes through which the sulphur trioxide was passed showed that, in the absence of finely divided solid matter, the sulphur trioxide was very stable and was not finally decomposed until a temperature of 1200° was reached (curve *D*). If, however, the tube was filled with any solid matter the substance was decomposed at a lower temperature as shown by curve *E*.

If the results obtained in such a process are plotted as in Fig. V., we can, by reference to the chart, determine what amount of contact mass will give the best yield at any given



Contact mass or time.

Fig. V.

temperature. The regions below 200° and above 900° to 1000° can be regarded as reactionless, while the best yield is obtained between 200° and 450°. Although the amount of product formed is not directly dependent upon the nature of the contact mass, yet the latter must be one which will give the greatest efficiency at about 450°. All substances which reach their highest efficiency above this temperature will never cause a quantitative yield, no matter how long the gases may be kept in contact, as they will be partly regenerated if they have first combined. The only substance which fulfils these conditions is platinum, even members of the same family not showing an equal efficiency. The introduction of this method has enabled the Badische Anilin- und Soda-Fabrik to increase the yield of the anhydride from 18,500 tons in 1888 to 116,000 tons in 1900.

At the close of the paper the author calls attention to the fact that such a piece of work could not have been carried out by an individual. It required the immense resources of such a company as the Badische Anilin- und Soda-Fabrik, directed by the far-reaching knowledge of Heinrich Brünck, the experience of Gustav Jacobsen, and the valuable aid of ingenious mechanics to carry it to success. J. Elliott Gilpin.

REVIEWS.

AN INTRODUCTION TO CHEMICAL ANALYSIS FOR STUDENTS OF MEDICINE, PHARMACY, AND DENTISTRY. By ELBERT W. ROCKWOOD, M.A., M.D., Professor of Chemistry and Toxicology in the College of Medicine, University of Iowa. Philadelphia: P. Blakiston's Son & Co. 1901.

This manual contains the regular course in qualitative inorganic analysis, tests for the common organic compounds including drugs and alkaloids, a section on volumetric analysis, chapters on the sanitary examination of water, the detection of poisons, and blowpipe analysis.

The book is well written; it is simple, clear, and explicit. Particular attention is called to the reactions of substances used as drugs. Pages of questions inserted at the end of the chapters emphasize reactions bearing on medicine or pharmacy and serve for self-examination.

Prof. Rockwood's manual is brief enough to be studied in the time given to laboratory work in the average medical school, and yet contains a surprising amount of sound practice. E. R.

KURZE ANLEITUNG ZUR QUALITATIVEN ANALYSE. Von DR. LUDWIG MEDICUS, Professor an der Universität Würzburg. Elfte Auflage. Tübingen, 1901. H. Laupp'sche Buchhandlung. Broschirt, M. 2; gebunden, M. 2.80.

That this is the eleventh edition of Prof. Medicus' Anleitung shows that the book retains the popularity won at its first appearance in 1877. The most noticeable change in the new edition is the brief treatise on solutions, mass reactions and chemical reactions in the light of physical-chemical theory, and the introduction into the text of brief explanations of single reactions in this sense.

This work occupies a position between the very brief manuals and the large text-books like that of Fresenius. It is full enough for most students. It gives the Bunsen flame reactions, and the reactions of the rare elements. It is deservedly popular. E. R.

HIGH-TEMPERATURE MEASUREMENTS. By H. LE CHATELIER, zugénieur en Chef du Corps des Mines, Professeur de Chimie Minerale au Collège de France, and O. BOUDOUARD, Assistant, Collège de France. Translated by GEORGE K. BURGESS, Instructor in Physics, University of Michigan. First edition, first thousand. New York: John Wiley & Sons; London: Chapman & Hall, Limited. pp. 230. 1901.

Attention has been turned recently to the measurement of very low rather than very high temperatures. This is due to

the fact that the low-boiling substances such as oxygen, air, nitrogen, and hydrogen can be obtained in the liquid form in any quantity desired. The measurement of very high temperatures has, however, not been disregarded, as is shown by the appearance of a volume like the one in hand. The author takes up the gas pyrometer, the calorimetric pyrometer, the electrical resistance pyrometer, the thermoelectric pyrometer, the heat-radiation pyrometer, the luminous-radiation pyrometer, the contraction pyrometer, fusible cones, and recording pyrometers.

The importance of high-temperature measurements is obvious to any one who has followed the work of Moissan, Le Chatelier, and Roberts-Austen. By means of the electric furnace Moissan has opened up an entirely new field for inorganic chemistry, and it is highly desirable to know, at least approximately, the temperatures at which these transformations take place. Le Chatelier has studied the electrical resistance of metals at very high temperatures, also their dilatation and allotropic transformations. He has shown that many new compounds probably exist at the more elevated temperatures. A number of allotropic modifications of iron and other elements have also been shown to exist by the work of Roberts-Austen. The applications of these extremely high temperatures have proved of incalculable service also in the industries.

The work needs no other commendation than that it was written by Le Chatelier. The English of the translation could, however, have been easily improved. H. C. J.

DIE NORMALELEMENTE UND IHRE ANWENDUNG IN DER ELEKTRISCHEN MESSTECHNIK. Von DR. W. JAEGER, Kaiserl. Professor, Mitglied der physikalisch-technischen Reichsanstalt in Charlottenburg. Verlag von Wilhelm Knapp, Halle A. S. pp. 131. 1902.

The information concerning normal elements is so scattered that it is often difficult to find what is desired. The problem is further complicated by the fact that such widely different results have been obtained with the same element by different experimenters. In the present volume we have the best that is known concerning this important class of cells.

The author takes up the theory of the normal element, discussing the relations between the intrinsic energy of the cell and its electromotive force, the dependence of the electromotive force upon the concentrations of the solutions, the temperature coefficient, and the osmotic theory of the normal element.

The several normal elements are then studied in detail. These include the following :

Daniell-Fleming element : $Zn - ZnSO_4 - CuSO_4 - Cu$.
Clark element : $Zn - ZnSO_4 - Hg_2SO_4 - Hg$.
Gouy element : $Zn - ZnSO_4 - HgO - Hg$.
Helmholtz-Ostwald element : $Zn - ZnCl_2 - Hg_2Cl_2 - Hg$.
Warren de la Rue element : $Zn - ZnCl_2 - AgCl - Ag$.
Weston element : $Cd - CdSO_4 - Hg_2SO_4 - Hg$.

The book concludes with a chapter on the measurement of the electromotive force of standard elements, and the use of such elements. The electromotive force of the Clark element as measured by the silver voltameter on the assumption that one ampere in a second separates from silver nitrate 0.001118 gram of silver is :

$$1.4328 - 0.00119\,(t - 15^\circ) - 0.000007\,(t - 15^\circ)^2 \text{ volt.}$$

The work comes from the best source in the world, *viz.*, the Reichsanstalt, and its author has contributed much to the subject upon which he is writing. It will certainly find its way into every laboratory where measurements of electromotive force are made. H. C. J.

SMOKELESS POWDER, NITROCELLULOSE, AND THEORY OF THE CELLULOSE MOLECULE. By JOHN B. BERNADOU, Lieutenant United States Navy. New York : John Wiley & Sons, 1901. 12 mo. pp. viii + 200. Price, $2.50.

As stated in the preface, the author " For purposes of comparative study . . . . . has brought together in the present volume a series of papers, by various investigators, upon the composition of cellulose and the properties of explosives prepared therefrom. He has supplemented these with an account of experiments made by himself, and from the whole has drawn certain conclusions as to the possible ultimate chemical composition of cellulose and the nitrocelluloses."

A general idea of the contents of the book can be obtained from the table of contents : Chapter I., Origin, Nomenclature, and Definitions ; Chapter II., Earlier Views as to Nitrocellulose Composition and Constitution ; Chapter III., The Conception of Progression in Relation to Composition and Constitution ; Chapter IV., Solutions of Nitrocellulose, Theory of the Cellulose Molecule. In the appendices the author has included translations of papers by Vieille and Bruley on " The Nitration of Cotton," one by Mendeléeff on " Pyrocollodion Smokeless Powders," and a sketch of his own work on the development of smokeless powders.

On account of the uncertainty regarding the exact composition of cellulose and its nitro compounds great confusion has arisen from the use of the same name for different substances, or different names for the same substance. The author gives exact definitions of the terms used by different writers and a

table of the synonyms. In tracing the historical development of the subject he shows how the investigators have been led to the conclusion that the cellulose molecule is more complex than had formerly been supposed, and the general course which the search for satisfactory smokeless powders has taken. Vieille has obtained eight nitrocelluloses, by working under different conditions, which differ in their solubility and stability.

The author has drawn conclusions regarding the composition and structure of cellulose from the action of solvents on the nitrocelluloses. It has been pointed out that the reactions of cellulose, in the cuprammonium, thiocarbonate, and mercerization processes, lead to the conclusion that the hydroxyl groups exist in both acid and basic form and that the solubility of the substance in a mixture of ether and alcohol at ordinary temperatures, while it will not dissolve in one alone, except at very low temperatures, is due to the different ways in which the two solvents act upon the hydroxyl groups, one acting upon the basic and the other upon the acid hydroxyl groups. Acting upon this suggestion, the author shows how a type unit of cellulose, represented by the composition $C_6H_{10}O_5$, which has four free single carbon bonds, could be written, and how the more complex polymeric forms could be built up of combinations of different numbers of these units. There is no limit to the possible number of such combinations, and the author suggests that by this assumption the definite chemical composition of the cellular form in the plant structure can be accounted for. He says that "the molecule need not be limited in composition to the simplest collection of the *lowest possible* number of atoms capable of entering into combination, but may be built up from a very great number of the elemental particles taken together in their proper ratios. Such a molecule would increase in amplitude according to the number of elemental particles entering into its composition; and the thought therefore suggests itself that *progressive variations in the amplitude of the molecular ring is a characteristic of organic life*, or conversely, that we may seek for the beginnings of organic life—at least in plant life—in the polymerization of the carbohydrates." He points out how, by the suggested structure, the polymerization, nitration, mercerization, and colloidation can be explained. The papers in the appendices by Mendeléeff, Vieille, and the author, who have been instrumental in developing the smokeless powders in use in the navies and armies of Russia, France, and the United States, respectively, give the general nature of the experiments of these experts, and furnish a valuable summary of results which have been difficult to obtain on account of

the secrecy maintained by the governments regarding this general subject. The author of this book is an expert on the subject, who is well qualified to present the matter in the clear and interesting form in which we find it here. Mendeléeff studied the theoretical conditions, which a satisfactory powder must fulfil, as regards safety from detonation, development of minimum heat and maximum propulsive effect, formation of little residue and keeping qualities, and, after studying many substances, finally suggested the use of pyrocollodion, as most successfully fulfilling all the requirements. The same explosive was independently developed in this country, and further improved by the addition of an oxygen carrier, so that the decomposition was not instantaneous, but similar to the effect of a number of subcharges exploding in succession and thus gradually increasing the velocity of the shot. Vieille and Bruley studied, in detail, the conditions influencing the formation of different nitrocelluloses, and were able to control fairly well the production of any desired compound.

J. E. G.

OUTLINES OF ELECTROCHEMISTRY. By HARRY C. JONES. D. Van Nostrand Co. 1901.

The contents of this little work is already familiar to many readers, having appeared as a series of papers under the title "Selected Chapters in Electrochemistry," in the *Electrical Review*, 1901. The author has aimed to present to engineers and others unfamiliar with the recent advances in physical chemistry a general idea of the fundamental principles on which modern electrochemistry is based. Although the work makes no pretense of being a systematic treatise on electrochemistry, all of the most important phases of the subject are touched upon, as will be seen from a synopsis of the contents, which includes chapters on Osmotic Pressure, The Electrolytic Dissociation Theory and Some of Its Applications, Electrolysis, The Velocity of Ions, Electrical Conductivity and Electromotive Force of Elements.

The reader will find these matters presented in a necessarily brief but, on the whole, admirably clear manner. Numerous references are made and long quotations taken from other works by the author. The natural tendency in an elementary discussion to make light of difficulties is sometimes apparent, and in several places a lack of proper balance between important and unimportant subjects is felt. For example, only about a page and a half are devoted to the question of the quantitative transformation of chemical into electrical energy —a matter of the greatest practical importance—while three chapters are devoted to the calculation of electromotive forces,

even the mathematical theory of liquid cells being worked out in some detail. The modern theories of electrolysis could have been made clearer if discussed subsequent to potential differences at metal-liquid junctions. The book fills, however, a real need, and can be heartily recommended to the class of readers for whom it is intended. It is unfortunate that the publishers have not seen fit to give it a more attractive form. It is to be hoped that the awkward size and arrangement of the page may be corrected in a later edition.

H. M. GOODWIN.

ON THE COMPOSITION OF DUTCH BUTTER. By J. J. L. VAN RYN, Director to the Royal Agricultural Experiment Station at Maastricht. London. 1902.

Owing to the fact "that Dutch butter, the origin of which placed its genuineness and purity beyond doubt, has been wrongly declared by foreign chemists to be a mixture of butter and margarine," the Netherlands government undertook a careful study of the case, and especially the conditions in the latter months of the year, as the trouble seemed to arise at that time. A very careful and exhaustive study of the conditions was carried out, and it was found, as here reported, that the conditions of feeding and pasturing, or "stabling," had a marked influence on the results, and showed that analytical results which are generally considered evidence of adulteration, could be obtained from specimens of pure butter under certain conditions of feeding, etc. J. E. G.

THE LABORATORY COMPANION TO FATS AND OILS INDUSTRIES. By J. LEWKOWITSCH, M.A., F.I.C. London: Macmillan & Co. 1901.

This book, by the author of the well-known work "Chemical Analysis of Oils, Fats and Waxes, Etc.," is almost exclusively devoted to tables which are of great value to any one working with fats and oils, as the information regarding these substances has been collected and tabulated in a very convenient form. The different values given in the literature have been carefully scrutinized and only the most reliable ones given. J. E. G.